



[LXXXVI]

[DECEMBER, 1914.]

# JOURNAL OF THE CHEMICAL SOCIETY

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LONDON:

HENEY AND JACKSON (SUCCESSORS TO J. VAN VOORST),  
33 PATERNOSTER ROW, E.C.

PRINTED IN GREAT BRITAIN BY R. CLAY AND SONS, LTD.,  
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#### CLIV.—*The Influence of Nitro-groups on the Reactivity of Substituents in the Benzene Nucleus.*

By JAMES KENNER.

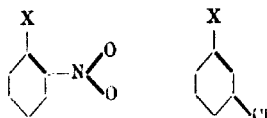
ALTHOUGH the enhanced reactivity of substituents in the ortho-para position relatively to a nitro-group has been a familiar fact since it was first observed by Pisani in the case of picryl bromide (*Lundén*, 1854, **92**, 326), little insight appears to have been gained into the nature of the processes which result in the placement of such substituents by others.

The "activating" influence of the nitro group is in direct contrast with its retarding, and at times inhibitive, effect on other reactions. Whilst, however, the nitro-group shares its power of retardance with other substituents of large molecular volume, irrespective of whether they are meta- or ortho- and para-directive, this is not the case where the opposite effect is concerned. In general, only meta-directive groupings can render substituents in the ortho position mobile; for instance, Schöpf and his pupils have found that the carboxy-, aldehydo-, sulphonic, and cyano-groups confer mobility on a bromine atom in the ortho- or para-position (*Ber.*, 1889, **22**, 900, 3281; 1890, **23**, 3440, 3445, 3450; **24**, 3771, 3785, 3808). The presence of a nitro-group was essential, but its influence was much more powerful than that of either groups named, and at least two of these, as compared with a single nitro-group in the ortho- or para position (compare *de Bruyn*, *Rec. trav. chim.*, 1894, **13**, 101), were required to render a substituent mobile. Ortho-para-directive substituents can, however, to increase the mobility of substituents in the meta position in some cases. Thus Laubenheimer showed that, instead of the conversion of *o*-dinitrobenzene into *o*-nitroaniline by action of alcoholic ammonia requires ten weeks at the ordinary temperature for its completion, the corresponding reaction in the case of 5-chloro-1:2-dinitrobenzene is complete within five days, and leads to the formation of 5-chloro-2-nitroaniline (*Ber.*, 1876, **9**, 1154, **11**, 1156).

Similarly, Tiemann found that *o*-chloro-*p*-nitrobenzaldehyde is converted into *o*-chloro-*p*-anisaldehyde by the action of sodium methoxide, *p*-nitrobenzaldehyde being stable in these circumstances (*Ber.*, 1891, **24**, 709). Attention has apparently not been hitherto directed to this phase of the problem, and it is therefore at present not possible to indicate how far this influence of the nitro atom is general, or shared by other ortho-para-directive substituents.

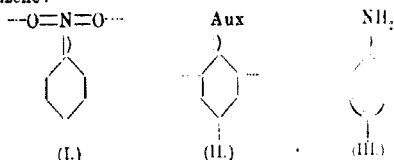
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The evidence as it stands, however, suggests a close connection between the phenomena at present under discussion and those of directive substitution; and, indeed, the various facts just enumerated find a ready explanation in terms of the views advocated by Flürscheim (*J. pr. Chem.*, 1902, [ii], **66**, 321; 1905, **71**, 497; 1907, **76**, 165, 185; T., 1909, **95**, 718; 1910, **97**, 84). Thus it is seen from the diagram that a nitro-group in the ortho- or para-position and a chlorine atom in the meta-position, each weaken the attachment of the substituent X to the nucleus, rendering it more mobile:



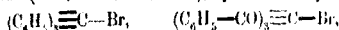
and that their influence is cumulative. Conversely, it may be expected that the effect of, for instance, a nitro-group in the meta-position, or a chlorine atom in the ortho- or para-position, may be a detrimental one. Quantitative experiments on the rates of such reactions are therefore desirable, in order to determine whether these influences exist, and, if so, whether they agree with those observed, for example, by Staudinger and Koenig (1912, **384**, 38), which are also capable of interpretation in the light of Flürscheim's views.

It must be remarked, however, that the attachment of a nitro-group to the benzene nucleus has been frequently assumed to be a comparatively strong one. Thus Kaufmann ("Die Auxochrome," Stuttgart, 1909, p. 76) refers to the aliphatic nature of the nitro-compounds, as illustrated by the reactivity of the aliphatic nitro-compounds, and later (p. 93) attributes the formula of nitrobenzene:

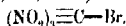


The adoption of this formula, preceded as it is (pp. 80, 81) by formulae II and III for benzene with the "ideal auxochrome" as a substituent, and for aniline, involves certain difficulties. Kaufmann is at once driven to attribute something in the nature of an amphoteric character to the phenyl residue, and to state "dass die Absättigung der Partialvalenzen bei Antiauxochromen polar zu der bei Auxochromen statthat." Further, it is pointed

has the presence of residual affinity on the ortho- and para-carbon atoms, as represented by Kaufmann, would tend to promote the substitution in the ortho- and para-positions which actually takes place. If, then, Kaufmann's formula for nitrobenzene be accepted, substitution might be expected to take the same course in this case, but this is not so. The strongest evidence in favour of Kaufmann's view is probably supplied by the work of Meisenheimer (*Annalen*, 1907, 323, 222; 1907, 355, 249), who examined very thoroughly the action of potassium methoxide on various nitro-compounds, and explained his results in terms of Thiele's theory of partial valencies. Making the same assumption in regard to the nitro-group as that made by Kaufmann. It will, however, be suggested that these results are not irreconcilable with the opposite point of view. Nor does Kaufmann's formula, in the author's opinion, a necessary consequence of Thiele's theory, which is based on a conception of the nature of the double bond uniting two atoms of the same element. Where a double bond connects two different elements, it is conceivable that one of these, that of greater residual affinity, may claim the whole of the available affinity of the other. This is especially so in the case of the nitro-group, where the single nitrogen atom is attached to two oxygen atoms, and if such were actually the case, Flürscheim's formula would represent nitrobenzene more accurately. Further, Werner's explanation of the activity and inertia of the respective halogen atoms in triphenylmethyl bromide and tribenzoyl-methane (*Ber.*, 1906, 39, 1282), symbolised by the formula:

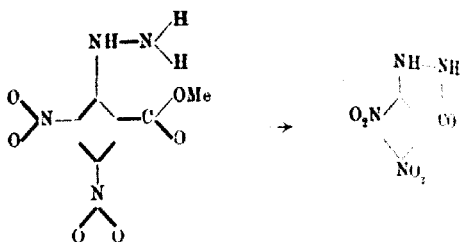


tends to lend support to the following formula for bromotribenzoyl-methane, the bromine atom of which is also inert (Meisenheimer and Schwarz, *Ber.*, 1906, 39, 2544):



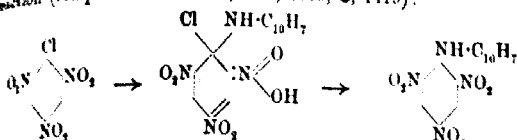
The evidence supplied by these considerations is therefore also in accordance with Flürscheim's views.

The following instance appears to show that the activating influence of nitro-groups may act through a chain of atoms, which do not form part of an aromatic nucleus. Whilst *o*-hydrazinobenzoic acid only passes over into 3-keto-1:3-dihydroindazole when heated alone to 220–230° or with boiling phosphoryl chloride (Fischer, *Ber.*, 1880, 13, 681; E. Fischer and Seuffert, *ibid.*, 1881, 14, 34, 795), methyl 3:5-dinitro-2-hydrazinobenzoate cannot be obtained as a product of the interaction of methyl 1-chloro-3:5-dinitrobenzoate and hydrazine hydrate, but is immediately converted into 3:5-dinitro-3-keto-1:3-dihydroindazole. The following scheme shows that this reaction is also in accordance with the views just stated:

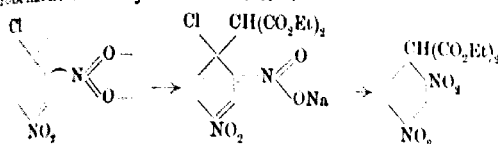


It might, however, be objected that, whereas Flürscheim<sup>4</sup> applied his views to explain the replacement of a hydrogen atom at the meta-position with respect to a nitro-group, they are here employed to explain the replacement of substituents in the meta or para-positions. This consideration is of great importance because it shows that, whatever the nature of the substituents, the processes involved in the two cases may be, they must be essentially different in character. Such a conclusion is supported by the fact that the steric hindrance of the negative groups in the ortho-position is to a large extent, although not completely, overcome by the fact that the nitro-group, which is the substituent most effective in exerting this hindrance, is also the most effective in promoting the condensation of the type under consideration. It seems clear that the activating group is itself concerned in the reaction. In view of the increasing favour with which the addition theory of diazo-reaction is now received, and of the fact that the nitro-group, especially prone to take part in the production of molecular compounds, it seems natural to assume that the formation of a molecular compound is the first step in the process at present under discussion: and, indeed, when an aromatic amine, for example, reacts with an active chloronitro-compound in alcoholic solution, an immediate coloration is at once produced which differs from that imparted to the alcohol by the final condensation product, and is probably to be attributed to the formation of an additive compound. This suggestion is not a novel one, and appears to have been first made by Bamberger (*Ber.*, 1900, **33**, 102), who, however, expressed no opinion as to the nature of the process by which the intermediate product passed over into the final condensation product. Bamberger actually isolated a molecular compound of picryl chloride and  $\alpha$ -naphthylamine, from which picryl- $\alpha$ -naphthylamine was formed; whilst Sudborough and Picton isolated similar molecular compounds of 4:6-dichloro-1:3-dinitrobenzene and of 2:4-dichloro-1:3:5-trinitrobenzene, each with one molecular proportion of  $\beta$ -naphthylamine (*T.*, 1906, **89**, 583). Sudborough and Pic-

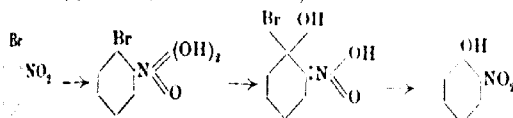
suggested the following scheme to explain the mechanism of the reaction (compare also Richter, *Ber.*, 1875, **8**, 1419):



But Borsche has recently (*Annalen*, 1911, **386**, 356; 1913, **402**, compare also Meisenheimer, *ibid.*, 1902, **323**, 218) advocated the following expression of the reaction between 4-chloro-1:3-dinitrobenzene and ethyl sodiomalonate\*:



apworth (P., 1903, **19**, 123; compare Meisenheimer and Patzig, *ibid.*, 1906, **39**, 253; Lobry de Bruyn, *Rec. trav. chim.*, 1904, **23**, suggested the formation of the same type of intermediate product, as a result of the passage of the substituting radicle from para to a  $\gamma$ -position (T., 1898, **73**, 445):



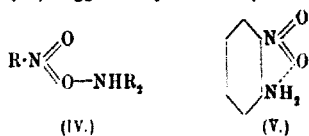
It is obvious that the whole question depends on that of the constitution of the molecular compounds first formed. The fact that 4-chloro-1:3-dinitrobenzene furnishes first ethyl 5-chloro-2:4-dinitro-malonate, only reacting with a further molecular proportion of ethyl sodiomalonate with much greater difficulty, and this unequal reactivity is considered to be an "experimental proof" of Kekulé's benzene formula, as against Thiele's or the *ortho* formula. It appears exceedingly doubtful whether this evidence is as reliable as that afforded by the work of Marckwald (*Annalen*, 1894, **279**, 5), for it is hardly convincing that evidence, which is interpreted with the assistance of his theory of partial valencies, should be used to disprove a formula which rests from an application of this theory to Kekulé's formula.

Further, it may be remarked that the formula of ethyl sodiomalonate used by Thiele is not the one generally adopted, and to this extent his choice of an expression for his theory is not a happy one.

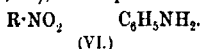
Thus, according to Borsche, the chlorine atom in the compound under discussion is loosely held. In this case it is difficult to account for the fact that Ullmann's theory of diphenyl derivatives by heating the haloid benzenes with copper powder is not applicable to chloro-compounds when they contain nitro-groups in the *ortho* or *para* position to the halogen atom (Ullmann and Bielecki, *Ber.*, 1907, **34**,



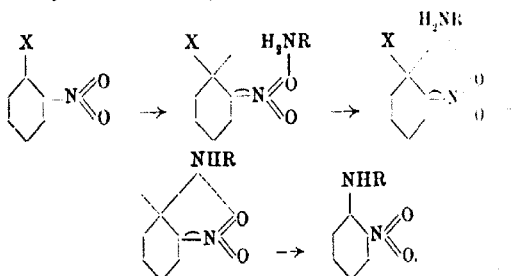
tetranitromethane and other aliphatic nitro-derivatives may be such compounds (Werner, *Ber.*, 1909, **42**, 4328) appears to be decisive evidence against a formula of the type postulated by Sudborough and Picton, and by Borsche, whilst Lapworth's formula supplies no explanation of the intense colour phenomena observed. The formula (IV) suggested by Werner (*loc. cit.*) is seen to be



closely related to that (V) adopted by Hantzsch for the azo-anilines (*Ber.*, 1910, **43**, 1669), and is in harmony with the observations of Sudborough and Beard (*T.*, 1910, **97**, 779), the substituents which tend to increase the auxochromic effect of the amino-group always tend to increase the depth of colour of the additive compounds of trinitrobenzene with amines (compare Green and Rowe, *T.*, 1912, **101**, 2446; Meldola and Healy, 1913, **103**, 884; Meldola and Hollely, this vol., p. 413). No attempt appears to have been made to institute a quantitative comparison by an examination of the absorption spectra of the two series of compounds, but it seems to the present author that this point requires attention before the alternative formula (VI), hinted at by Picton (*Annalen*, 1914, **404**, 13), is accepted:



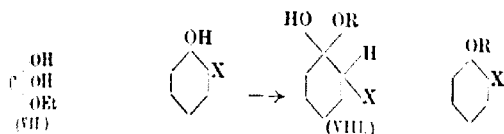
Meanwhile, Werner's formula has been retained in the following attempt to depict in outline the course of the reaction by which an arylamino-radical displaces a mobile substituent X:



As a consequence of the formation of the molecular compound, a certain amount of unsatisfied valency may be expected momentarily to exist, as shown, on the carbon atom to which X is attached,

either be absorbed by X or engage a portion of the residual energy of the spatially proximate nitrogen atom. Of the two alternatives, the latter, represented by the third formula in the *loc. cit.*, seems the more probable because it enables the system, by subsequent rearrangement in the manner indicated, to attain a condition of smaller potential energy.

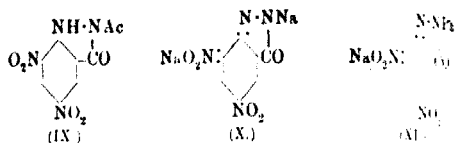
The process by which the nitro-group facilitates the condensation thus considered to consist in rendering it intra- rather than intermolecular by bringing the amino molecule into a position favourable to the formation of a five-membered ring (or, if Pfeiffer's formula were adopted, of a six-membered ring). It is this feature which differentiates the views now put forward from those of Pfeiffer; whilst, in the author's opinion, the supporters of the latter theory are confronted with the dilemma that the steric distance of groups is probably explicable in a manner substantially similar to that by which they seek to explain the opposite effect. Thus Henry's theory, that esterification depends on the formation of the intermediate compound (VII), has been extended



to the case of the phenols, it being assumed that a sterically active group X prevents the formation of the intermediate additive compound (VIII) (*Monatsh.*, 1895, **16**, 140; compare also Davies, T., 1900, **77**, 33). The theory, that this is the mode of formation of substitution derivatives of phenol, has been current for a considerable time, and is strongly supported by experimental evidence recently adduced (Meyer and Lenhardt, *Ber.*, 1913, **398**, 51; Meyer, Irseich and Schlösser, *Ber.*, 1914, **171**; compare Auwers and Michaelis, *ibid.*, p. 1275). From this connexion attention may be drawn to the behaviour of an amine. This amine furnishes a reddish-brown explosive potassium salt (Green and Rowe, T., 1913, **103**, 513), but is attacked by an anhydride only in the presence of sulphuric acid\* (Witt and *Ber.*, 1908, **41**, 3092; compare Paal and Benker, *Ber.*, 1899, **1251**; Paal and Härtel, *ibid.*, p. 2051; Meldola and Höllely, *ibid.*, p. 410). Similarly, 5:7-dinitro-3-keto-1:3-dihydroindazole

\* It is noteworthy that sulphuric acid has also been found to be effective in accelerating the esterification of acids which remain unaffected under the usual conditions (Wegscheider, *Ber.*, 1895, **28**, 3128; Kenner and Mathews, this vol., p. 1).

furnished a *monoacetyl* derivative (IX), and a deep brown *additive diacid* salt (X), whereas its 2-phenyl derivative *only* was acetylated, and only yielded a *monosodium salt*\* (XI). It thus appears that the hydrogen atom in position (1) cannot be replaced under ordinary conditions, but can take part in salt formation. Since a diacetyl derivative and a monosodium salt are obtained from 3-keto-1:3-dihydroindazole itself, it is clear that its relationship in these respects to its dinitro-derivative corresponds exactly with that of aniline to picramide:



These examples illustrate the fact that a nitro-group can render an amino-group by steric hindrance, and yet render it highly active towards alkali. In other words, the two groups involved, of which one is a particular example of those with which this paper is concerned, are fundamentally different.

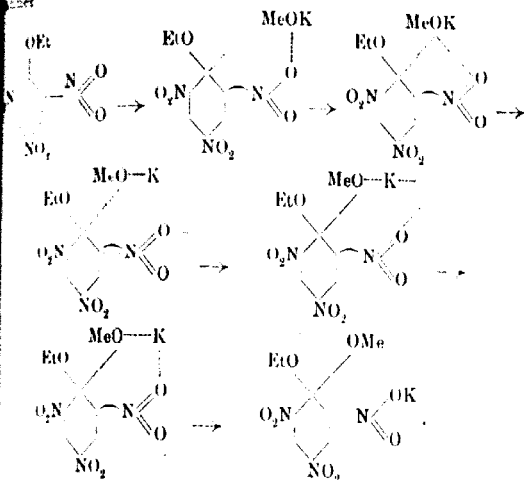
A group of large molecular volume occupying the second position to the substituent X may, of course, be expected to exercise the steric hindrance usually observed in such cases in the formation, and we therefore find that 2-chloro-1:3-dinitrobenzene reacts much less rapidly than 4-chloro-1:3-dinitrobenzene (Blaschke and Rantsch, *Annalen*, 1911, **379**, 152). Steric hindrance must further be considered in regard to their effect on the formation of the primary additive compound. Thus Sauer and Picton (*loc. cit.*) showed that the introduction of three or two methoxyl groups, or three bromine atoms into the ring of trinitrobenzene completely inhibited the formation of such compounds with  $\alpha$ - or  $\beta$ -naphthylamine, whilst Hofmann and Kauter found that alcoholic solutions of trinitroresorcinol or trinitro-*m*-xylene, in contrast with trinitrobenzene, developed colour when hydrazine hydrate was added (*Ber.*, 1910, **33**, 17). Similarly, Jackson and Boos showed that di- and trinitrotoluenes did not give coloured additive products with metallic oxides (*Amer. Chem. J.*, 1898, **20**, 444). The importance of this factor is illustrated by the case of 4:6-dibromo-1:2-dinitrobenzene from which the 1-nitro-group is displaced by the amino-group (Blanksma, *Rec. trav. chim.*, 1908, **27**, 50):

\* The formulæ given to these salts in the text are of course alternative to the quinonoid ones, or to Hantzsch's *aci*-formulæ.

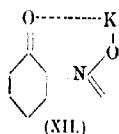


A comparison with the behaviour, already quoted, of 4-chloro-(trime-)1:2-dinitrobenzene at once suggests that the nitro-group in position 2 would be the more easily displaced were it not that the other nitro-group is sterically prevented from forming the necessary additive compound.

The above considerations are applicable in other cases. Thus, the reaction between potassium methoxide and trinitrophenetole (Lebenheimer, *loc. cit.*) may be represented in the following manner:

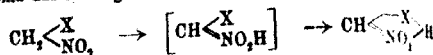


Formation of coloured salts of nitrophenols, to which Hantzsch assigned the formula (XII) (*Ber.*, 1912, **45**, 90), can be expressed in the same manner:

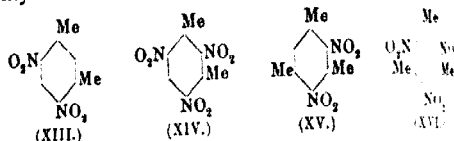


It is no longer remarkable that "echte Nitrokörper mit einer starken negativen Gruppe isomerisieren sich als Pseudosäuren (durch Alkalien) niemals nur zur ersten Stufe der einfachen

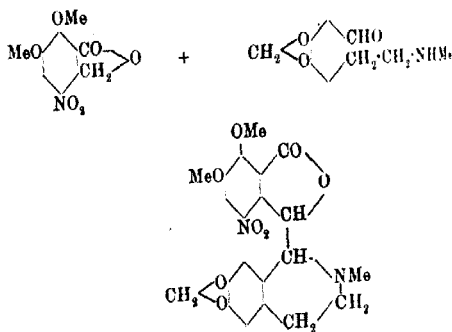
*aci*-Nitrokörper, sondern stets sofort zu der zweiten Stufe der kondensierten *aci*-Nitrokörper, so dass in dem folgenden Umlagerungsschema das Mittelglied nicht existiert" (Hantzsch, *loc. cit.*)



The course of the condensation of 2:4-dinitrotoluene with benzaldehyde in presence of secondary bases (Thiele and Escala, *Ber.* 1901, **34**, 2842) may perhaps be considered to take place in a similar manner. This suggestion at once accounts for the observations made by Borsche (*Annalen*, 1911, **386**, 351), who was unable to explain. Whilst 4:6-dinitro-(XIII) and 2:4:6-trinitro-(XIV)-*m*-xylenes respectively give yields of 43 per cent. of the corresponding distyrylbenzenes when condensed with benzaldehyde, 2:4-dinitro-(XV) and 2:4:6-trinitro-(XVI)-*m*-xylenes are unchanged.



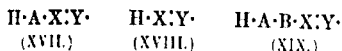
In the last two cases the nitro-groups are sterically prevented from forming the required additive compound, but in the first two cases both the 4- and the 6-nitro-groups are free to do so. However, the condensation took place by direct interaction of the nitro-groups with the aldehydes, trinitro-*m*-xylene should be unchanged as trinitromesitylene is, whilst dinitromesitylene should react in the same case. Also, a comparison of the behaviour of the two trinitro compounds is interesting as illustrating the resultant influence of



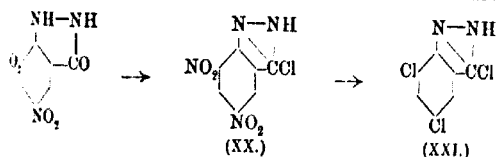
one hand the activating influence, and on the other the steric  
 hindrance to the later stages of the reaction, of the 2-nitro-group.  
 Further, it may be observed that Hope and Robinson, when con-  
 sidering the mechanism of the condensation of nitroacetone with  
 formaldehyde (shown on p. 2726), attributed two functions to the  
 nitro-group: "first, in attracting the nitro-compound and in  
 forming a loose combination of the type of the compounds obtained  
 with amines and trinitrobenzene, and secondly, in effecting the  
 condensation between the aldehyde and methylene groups" (T.,  
 1909, 1153, 2114). The views thus expressed approximate very  
 closely to those advocated above.

The reactivity induced by other meta-directive groups may  
 similarly be explained in a similar manner. Thus there is abundant  
 evidence that the carbonyl group is able to take part in the forma-  
 tion of molecular compounds (compare, for example, Pfeiffer,  
*Monatsh.*, 1910, **376**, 285; 1911, **383**, 92; *Ber.*, 1914, **47**, 1580),  
 and it is probable that the same will be found to be true of the  
 nitril and the cyanogen groups.

It is possible that similar considerations might lead to an  
 explanation of the activity of the chlorine atom and the methyl  
 group in 2-chloro- and 2-methyl-pyridines. At any rate, these  
 examples serve to expose the inaccuracy of Vorländer's statement  
 (*Monatsh.*, 1910, **320**, 66), according to which the "reactive" un-  
 saturated group,  $\cdot X:Y \cdot$ , causes mobility of the hydrogen atom in  
 position XVII, but not in XVIII or XIX:

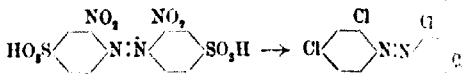


Whilst, however, the views just developed suffice to explain a  
 number of observed facts, they do not embrace another reaction,  
 which was observed during the course of the experiments about  
 to be described. Thus it was found that 3-chloro-5:7-dinitroindazole  
 is formed when 5:7-dinitro-3-keto-1:3-dihydroindazole is  
 heated under pressure with phosphoryl chloride at 140°, is converted  
 into 3,5,7-trichloroindazole (XXI) if the reaction is carried out  
 in benzene, and the 2-phenyl derivative showed a similar behaviour:



Analogous observations have been made by Lobry de Bruyn  
 (*Ann. chim.*, 1896, **15**, 84), who found that, among others,

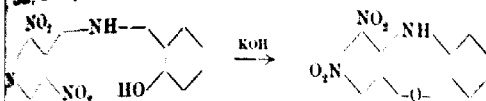
*p*-trinitrobenzene and the three dinitrobenzenes were converted into the corresponding chloro-derivatives when heated with concentrated hydrogen chloride solution at 200—300°. Similarly Zander and Kuchenbecker (*Annalen*, 1904, **330**, 50) showed that 2,4-dinitroazobenzene-4'-disulphonic acid, when heated with concentrated hydrochloric acid at 160°, furnished tetrachloroazobenzene.



The facts that all the nitro-groups are displaced, and that in all cases of the dinitrobenzenes the reaction is independent of the orientation, would appear to indicate that the cause of the reaction is to be sought in the relationship of the nitro-groups to the benzene nucleus rather than in any direct mutual influence of the groups. Since, however, nitrobenzene itself does not undergo reaction (Lobry de Bruyn and van Leent, *loc. cit.*), it is clear that the second nitro-group does play some part, probably suitably modifying the condition of the benzene nucleus. We surmise receives some measure of support from the fact that displacement of nitro-groups by chlorine atoms takes place more readily in the case of naphthalene derivatives (Angew. *Ber.*, 1876, **9**, 1187, 1732; 1877, **10**, 1843), in which the nature of the nuclei is generally acknowledged to be somewhat different from that of the ordinary benzene nucleus. This idea is also supported for it is implied in the term "negativity," by which the theory of organic chemistry dealing with such cases of mobility is sometimes designated. It is therefore also probable that the effect of nitro-groups on the benzene nucleus must be taken into account in connexion with the reactions to which the main part of the present discussion has been devoted. Similarly, the nature of the substituent to be replaced also requires consideration. Thus, St. John and Picton were unable to prepare picryl-naphthalene from picrylaniline, although the necessary additive compound was isolated (*loc. cit.*, p. 587). The fact that *p*-trinitrobenzene is converted into 3:5-dinitroanisole by the action of sodium but is not affected by ammonia (Lobry de Bruyn, *Rec. trav. chim.*, 1890, **9**, 214, 218; 1894, **13**, 148), shows that the nature of the entrant group is also of importance. It must, however, be noted that these factors operate by predisposing the system to react rather than by playing any active part in the change.

Still other influences are noticeable in certain cases. Thus, the displacement of a nitro-group in the course of the synthesis of 3:5-dinitro-oxazine from 2:4:6-trinitro-2'-hydroxydiphenylamine

prepared by Turpin (T., 1891, 59, 722; see also Kehrmann, *Ber.*, 33, 2605):



comparable with the conversion, just cited, of *o*-trinitrobenzene to 5-dinitroanisole, and is probably a result of the negativity of the benzene nucleus. This, however, affords no explanation of the observed by Ullmann, that whilst Turpin's reaction is applicable to 2:6-dinitro-2'-hydroxydiphenylamine, it fails in the case of 1:4-isomeride (*Annalen*, 1909, 366, 79).

Further, the result of the action of potassium cyanide on alcoholic solutions of the bromonitrobenzenes and similar compounds at 180°, studied by Richter, is remarkable. Para- and meta-bromonitrobenzenes are respectively converted into meta- and ortho-bromobenzoic acids, but the ortho-isomeride is recovered unchanged (*Ber.*, 1871, 4, 21, 461, 553; 1874, 7, 1145; 1875, 8, compare Zincke, *Ber.*, 1874, 7, 1503). Whilst these reactions are formal in the sense that the hydrogen atom in the ortho-position to the nitro-group is attacked in each case, they disclose a tendency, not observed in any of the cases previously referred to, on the part of the substituting group (in this case oxygen, which is subsequently hydrolysed), to enter the nucleus as well as the other negative group as possible. So strong is this tendency that it prevents the conversion of *o*-bromonitrobenzene into *o*-bromobenzoic acid, although both the bromine atom and the nitro-group in this case conduce to the mobility of the meta-hydrogen; whilst in the second case quoted above the reaction takes place irrespective of considerations of steric hindrance, which would make the para-hydrogen atom as more likely to be attacked.\* If allowance is made for this factor, the action of potassium cyanide on various nitro-compounds, apparently so bewildering in the variety of results observed (collated by Lobry de Bruyn, *Rec. chim.*, 1904, 23, 47), affords an excellent illustration of the effect of the influences previously discussed, namely:

- (1) the loosening influence of meta-directive groupings on ortho-para-substituents;
- (2) the corresponding effect of ortho-para-directive groups on ortho-substituents;

Notably bromonitrobenzonitriles are first produced in this reaction. For a study of the mobility of the nitro-group in such compounds, compare the cases of *o*-cyanonitrile, *m*-dinitrobenzene, and other compounds referred to later.



(c) steric hindrance to the formation of the initial compound and to the attack of otherwise mobile groups;

(d) the negative condition of the benzene nucleus;

(e) the nature of the substituent to be replaced and of the entrant group. It will be observed that, in the following cases, nitro-groups attached to a negative nucleus and hydrogen atoms alone suffer displacement. Halogen atoms are not affected by potassium cyanide.

The following table shows the more notable of the results obtained in this direction, accompanied by references to the literature summary:

Nitro-compound.	Conditions employed.	Product.	Influences.	References to literature.
<i>o</i> -Dinitrobenzene.	Alcoholic solution at 170°.	No change.	†	Bruyn and van der Broek, <i>Rec. trav. chim.</i> , 1899, 18, 330.
<i>p</i> -Dinitrobenzene.	Boiling alcoholic solution.	<i>p</i> -Nitroanisole.	(a) + (d).	Bruyn and van der Broek, <i>ibid.</i> , 1899, 18, 331.
<i>m</i> -Dinitrobenzene.	Boiling alcoholic solution.	[2:6-Dinitrobenzonitrile] → 6-nitro-2-methoxybenzonitrile.*	(a) + (d).	Bruyn and van der Broek, <i>ibid.</i> , 1899, 18, 332.
Dinitrated 6-nitro-2-ethoxybenzonitrile.	Warm alcoholic solution.	A dinitrile, the 6-nitro-group being displaced.	(a) + (b) + (d).	van Hogen, <i>ibid.</i> , 1900, 19, 424.
1:2:4-Tri-nitrobenzene.	Boiling alcoholic solution.	2:4-Dinitroanisole.	(a) + (d).†	Bruyn, <i>ibid.</i> , 1899, 18, 331.
4-Chloro-1:3-dinitrobenzene.	Boiling alcoholic solution.	5-Chloro-6-nitro-2-methoxybenzonitrile.	(a) + (b) + (d) + (c).	van Hogen, <i>ibid.</i> , 1900, 19, 424.

\* The cyanogen group renders a nitro-group in the ortho-position (influences (a) + (d)). Thus *o*- and *p*-nitrobenzonitriles, when boiled with a solution of sodium methoxide, are converted into *o*- and *p*-methoxybenzonitriles. *Rec. trav. chim.*, 1899, 18, 330; Keluders and Ringer, *ibid.*, 1900, 19, 424. It is noted that some *o*-nitroanisole is also produced in the former case (*ibid.*, 1900, 19, 424). Further, Lobry de Bruyn showed that 2-methoxy-6-nitrobenzonitrile is converted into 2:6-dimethoxybenzonitrile by methyl-alcoholic potassium cyanide (*Rec. trav. chim.*, 1893, 2, 205).

† The 1-nitro group diminishes the mobility of the 3-hydrogen atom, and prevents the reaction from following a similar course to that observed in the case of *m*-dinitrobenzene. The influence of the chlorine atom and the ammonium salt cases next quoted is, however, in favour of such a result. This influence of the chlorine atom is clearly responsible for the partial conversion of 4:4-

Re- sponse	Conditions employed.	Product.	Influences.	References to literature.
Intro- duc-	Alcoholic so- lution at 60°.	2:6-Dinitro-3- aminophenol.	(a) + (b) + (c) + (e).	Lippmann and Fleis- ner, <i>Monatsh.</i> , 1885, 6, 807; 1886, 7, 95.
Ex- trac-	Aqueous solu- tion at 35° (Nietzki and Petri).	Potassium iso- purpurate.*	(a) + (b) + (c) + (e).	Nietzki and Petri, <i>Ber.</i> , 1900, 33, 1788; Borsche, <i>Ber.</i> , 1900, 33, 2718, 2995; Borsche and Locatelli, <i>Ber.</i> , 1902, 35, 569; Borsche and Becker, <i>Ber.</i> , 1903, 36, 4357; Bruyn, <i>Rec. trav.</i> <i>chim.</i> , 1904, 23, 56. Blanksma, <i>Rec. trav.</i> <i>chim.</i> , 1901, 20, 411, 423.
4 (in- ter- med- iate)	—	No change.	(c).	

2-nitrobenzene into 3-chloro-5-nitroanisole by the action of sodium methoxide,  
2-dinitrobenzene is simply reduced (Kock, *Rec. trav. chim.*, 1901, 20, 111;  
*ibid.*, 1899, 18, 13).

The authorities quoted agree that isopurpuric acid contains cyanogen groups in  
the 2- and 6-positions, but differ in regard to the fate of the 2- and 6-nitro-groups.  
Lobry de Bruyn and Nietzki and Petri, one of them is converted into an amino-group, whilst  
the other remains unchanged.

Lobry de Bruyn considers that the colour of the compound would be  
explained by the presence of a nitroso- and a hydroxylamino-group in place  
of the two nitro groups. The question as to the extent to which the nitro groups  
are reduced has, however, no bearing on the present discussion.

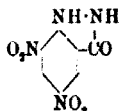
Two points in connexion with the above table call for explana-

No attempt is made to explain the introduction at one time  
of a cyanogen group, at another of an alkyloxy-group, as a result  
of the action of potassium cyanide. This problem, which lies out-  
side the scope of the present discussion, was considered by Lobry  
de Bruyn, who, however, was unable to arrive at any very definite  
conclusion (*Rec. trav. chim.*, 1904, 23, 47). Also, the term  
"influences" at the head of one column of the table is only meant  
to comprehend those which would appear to play a decisive part  
in determining the final result.

## EXPERIMENTAL

[With RAYMOND CURTIS.]

## 5:7-Dinitro-3-keto-1:3-dihydroindazole,



An alcoholic solution of hydrazine hydrate (6 grams) cautiously added to a solution of methyl 2-chloro-3-benzoylbenzoate (10 grams) in warm alcohol (100 c.c.). Each time caused a vigorous reaction, which became violent if the temperature was too high, and a dark red hydrazine salt immediately precipitated. After dilute hydrochloric acid had been added to the mixture, the free indazole derivative was separated and purified by crystallisation from glacial acetic acid. It separated from the solution in yellow, hexagonal plates, melting and decomposing at about  $300^\circ$ :

0.1900 gave 0.2596  $\text{CO}_2$  and 0.0368  $\text{H}_2\text{O}$ .  $\text{C}=37.26$ ;  $\text{H}=1.736$ .

0.1736 " 38.2 c.c.  $\text{N}_2$  at  $17^\circ$  and 734 mm.  $\text{N}=25.00$ .

$\text{C}_7\text{H}_4\text{O}_5\text{N}_4$  requires  $\text{C}=37.50$ ;  $\text{H}=1.78$ ;  $\text{N}=25.00$  per cent.

The compound was not appreciably soluble in cold alcohol, in benzene, or chloroform; it was fairly soluble in boiling alcohol, readily so in glacial acetic acid or acetic anhydride.

The disodium salt was prepared by triturating 5:7-dinitro-keto-1:3-dihydroindazole (2 grams) with 5*N*-sodium hyposulfite solution (7 c.c.). After the addition of absolute alcohol (5 c.c.) to the resulting deep brown paste, the salt was collected, washed with absolute alcohol until the washings were free of alkali. For analysis two different specimens were prepared, the second by the use of a considerable excess of sodium hyposulfite solution; although the products were dried at  $130^\circ$ , the salt retained two molecular proportions of water:

0.1288 gave 0.0603  $\text{Na}_2\text{SO}_4$ .  $\text{Na}=15.17$ .

0.2938 " 0.1380  $\text{Na}_2\text{SO}_4$ .  $\text{Na}=15.22$ .

0.134 required 9.2 c.c.  $N/10\text{-H}_2\text{SO}_4$ .  $\text{M.W.}=291.8$ .

$\text{C}_7\text{H}_2\text{O}_5\text{N}_4\text{Na}_2\cdot 2\text{H}_2\text{O}$  requires  $\text{Na}=15.13$  per cent.;  $\text{M.W.}=292$ .

The salt exploded when heated, and this prevented determinations of its other elements being made. It was readily soluble

\* The salt itself served as indicator in the titration. Owing to the explosion determining the exact end-point, no claim can be made for great accuracy of result.

er, soluble in alcohol or acetone, but insoluble in benzene or reform. By treating its aqueous solution with suitable reagents, a reddish *ferrie* salt, an insoluble dark brown *silver* salt, a moderately soluble dark brown *copper* salt were obtained. The *monoacetyl* derivative separated in greenish-yellow crystals from the solution obtained by boiling the compound (2 grams) with acetic anhydride (5 grams) for eight hours. It crystallised from glacial acetic acid in rectangular prisms, melting at 200°.

1701 gave 0.2548 CO<sub>2</sub> and 0.0340 H<sub>2</sub>O. C=40.85; H=2.22.

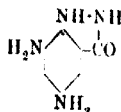
1548 " 28.6 c.c. N<sub>2</sub> at 18° and 741 mm. N=21.2.

C<sub>10</sub>H<sub>6</sub>N<sub>4</sub> requires C=40.60; H=2.25; N=21.05 per cent.

The solubility relationships of the acetyl derivative corresponded to those of the parent substance. It was soluble in alkali, forming a deep red solution.

Attempts to prepare a diacetyl derivative were fruitless, the acetyl derivative being produced in every case.

5: 7-Diamino-3-keto-1: 3-dihydroindazole.

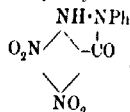


A dinitro-derivative (4 grams) was added to a solution of stannous chloride in glacial acetic acid (80 grams), saturated with hydrogen chloride. After twelve hours, the reduction product was removed from the precipitate by treatment with hydrogen sulphide in the usual manner. It was analysed in the form of its *oxalate*, which was precipitated when ammonium oxalate was added to an aqueous solution of the hydrochloride of the base:

1701 gave 20.8 c.c. N<sub>2</sub> at 18° and 740 mm. N=21.95.

C<sub>10</sub>H<sub>6</sub>ON<sub>4</sub>.C<sub>2</sub>H<sub>2</sub>O<sub>4</sub> requires N=22.20 per cent.

5: 7-Dinitro-3-keto-2-phenyl-1: 3-dihydroindazole.



An alcoholic solution of phenylhydrazine (12 grams) was slowly added to a warm solution of methyl 2-chloro-3: 5-dinitrobenzoate (100 c.c.) in alcohol (100 c.c.). After the mixture had been stirred in the water-bath for fifteen minutes, it was worked up as usual.

in the previous case. The product consisted of two compounds, one of which was extracted by boiling alcohol. The residue (90—95 per cent. of the yield) crystallized from glacial acetic acid in flat needles, which melted and decomposed between 220° and 250°:

0.1814 gave 0.3464  $\text{CO}_2$  and 0.0477  $\text{H}_2\text{O}$ .  $\text{C} = 52.08$ ,  $\text{H} = 2.22$

0.1552 „ 25.2 c.c.  $\text{N}_2$  at 16.5° and 740 mm.  $\text{N} = 18.66$

$\text{C}_{13}\text{H}_8\text{O}_5\text{N}_4$  requires  $\text{C} = 52.00$ ;  $\text{H} = 2.66$ ;  $\text{N} = 18.66$  per cent.

The compound was therefore either the 1- or the 2-phenyl derivative of 5:7-dinitro-3-keto-1:3-dihydroindazole. It was sparingly soluble in boiling alcohol, benzene, or chloroform; was moderately soluble in glacial acetic acid and in epichlorohydrin.

The monosodium salt was obtained as an amorphous powder in the manner already described in the case of dinitroketodihydroindazole, and exhibited a similar tendency to explode when heated. It was readily soluble in water, soluble in alcohol or acetic acid, insoluble in chloroform or benzene:

0.2162 gave 0.0491  $\text{Na}_2\text{SO}_4$ .  $\text{Na} = 7.35$ .

0.1610 required 5.0 c.c.  $\text{N}/10\text{-H}_2\text{SO}_4$ .  $\text{M.W.} = 322$

$\text{C}_{13}\text{H}_7\text{O}_5\text{N}_4\text{Na}$  requires  $\text{Na} = 7.1$  per cent.;  $\text{M.W.} = 322$

By double decomposition with its aqueous solution, an insoluble deep red silver salt, and a moderately soluble, brown copper salt, were obtained. The compound is insufficiently acidic to permit the formation of a ferric salt.

Attempts to prepare an acetyl derivative by various means were unsuccessful, the original compound being recovered in each case. A colourless substance separated from the solution after adding sulphuric acid to a mixture of the compound with its anhydride, but it decomposed and turned yellow immediately on coming in contact with the moisture of the atmosphere.

As explained in the introduction, these reactions agree with the behaviour of picramide, and it is therefore considered that the compound is a 2-phenyl derivative. This conclusion is in accordance with the results of E. Fischer (*Annalen*, 1878, 190). Fischer showed that the condensation of picryl chloride with hydrazine results in the formation of trinitrohydrazobenzene; it appears that other products may result under slightly different conditions (Willgerodt and Ferko, *J. pr. Chem.*, 1888, [iii], 37). Fischer, *Annalen*, 1889, 253, 1, and Fischer himself showed that a mixture of symmetrical and unsymmetrical derivatives is produced by the action of alkyl bromides on phenylhydrazine; compare also Michaelis and Schmidt, *Ber.*, 1887, 20, 43). These facts may throw some light on the formation in the present case.

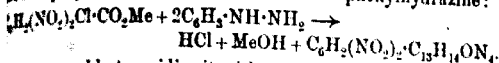
and compound, which was deposited from the above-mentioned alcoholic solution in yellow, rhomboidal plates. After repeated crystallisation from alcohol, the compound melted at  $175^{\circ}$ :

1420 gave 0.2897  $\text{CO}_2$  and 0.0502  $\text{H}_2\text{O}$ .  $\text{C}=55.64$ ;  $\text{H}=3.93$ .

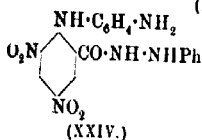
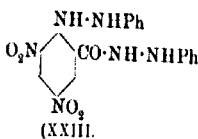
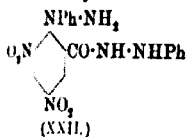
1450 .. 25.6 c.c.  $\text{N}_2$  at  $16^{\circ}$  and 737 mm.  $\text{N}=20.51$ .

$\text{H}_8\text{O}_4\text{N}_4$  requires  $\text{C}=55.89$ ;  $\text{H}=3.92$ ;  $\text{N}=20.60$  per cent.

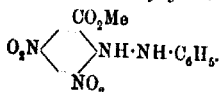
The compound therefore resulted from the condensation of one molecular proportion of the ester with two of phenylhydrazine:



We were unable to oxidise it with mercuric oxide, to condense it with aldehydes, to convert it into the indazole derivative produced simultaneously with it, or to prepare it from 2:4-dinitro-6-carbomethoxyhydrazobenzene. Unless steric influences be assumed, this case is at variance with the possible formulae XXII and XXIII, whilst formula XXIV, representing the product of the direct inversion of XXIII, is rendered improbable by the fact the compound in question may be isolated without the aid of phenylhydrazine, by removing the phenylhydrazine salt of dinitroketophenylindazole by solution in cold alcohol:



2:4-Dinitro-6-carbomethoxyhydrazobenzene,



phenylhydrazine (8 grams) had been added to a solution of ethyl 2-chloro-3:5-dinitrobenzoate (10 grams) in alcohol (4), the mixture was heated to the boiling point, and then filtered. The precipitate thus obtained was warmed with alcohol, after filtration, the solution deposited orange crystals of the derivative. After further crystallisation from warm alcohol, it melted at  $144-145^{\circ}$ :

0.1634 gave 0.3016  $\text{CO}_2$  and 0.0523  $\text{H}_2\text{O}$ .  $\text{C}=50.45$ ;  $\text{H}=3.1$   
 0.1430 „ 21.7 c.c.  $\text{N}_2$  at  $20^\circ$  and 732 mm.  $\text{N}=17.11$

$\text{C}_{14}\text{H}_{13}\text{O}_6\text{N}_4$  requires  $\text{C}=50.60$ ;  $\text{H}=3.61$ ;  $\text{N}=16.87$  per cent.

When its alcoholic solution was boiled for a few minutes, no condensation took place, and the corresponding dihydrazide derivative was precipitated. The same product was obtained in attempts were made to condense the hydrazo-derivative with phenylhydrazine or benzaldehyde.

*s-2:4:2':4'-Tetranitro-6:6'-dicarbomethoxytetraphenylhydrazine*,



An alcoholic solution of hydrazobenzene (2 grams) was mixed with a solution of methyl 2-chloro-3:5-dinitrobenzoate (5 g.) in alcohol (60 c.c.) on the water-bath for one hour. The precipitate, after filtration and crystallisation from nitrobenzene, melted at above  $340^\circ$ :

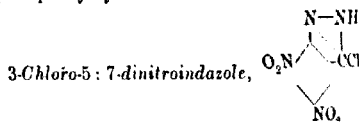
0.1777 gave 0.3480  $\text{CO}_2$  and 0.0526  $\text{H}_2\text{O}$ .  $\text{C}=53.40$ ;  $\text{H}=3.1$

0.1918 „ 21.6 c.c.  $\text{N}_2$  at  $20^\circ$  and 747 mm.  $\text{N}=12.34$

$\text{C}_{28}\text{H}_{20}\text{O}_{12}\text{N}_6$  requires  $\text{C}=53.16$ ;  $\text{H}=3.16$ ;  $\text{N}=13.29$  per cent.

It was insoluble in alkalis, and in most organic solvents, nitrobenzene and epichlorohydrin. Attempts to hydrolyse the compound with acid or with alkali were unsuccessful.

If the constitution assigned to the phenylindazole derivative already described, is accepted, it is remarkable that the phenylamino-group of hydrazobenzene reacts with a second molecule of ester rather than with the carbomethoxyl group of the molecule, and it might be suggested that this is evidence in favor of the alternative constitution. On the other hand, however, it may be argued that the velocity of reaction in the present case is much slower than when phenylhydrazine is used, and that this is due to the greater facility with which the ester condenses with the amino-group of phenylhydrazine.



5:7-Dinitro-3-keto-1:3-dihydroindazole (5 grams) was mixed with phosphoryl chloride (35 grams) for four hours under pressure at  $120-140^\circ$ . After the excess of phosphoryl chloride had been removed by warming the product under diminished pressure

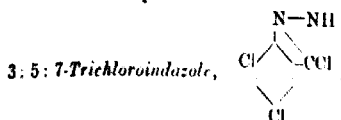
was stirred with water, collected, and repeatedly crystallized from glacial acetic acid. In this way, yellow needles (grams) were obtained, which melted at  $179-180^{\circ}$ :

1994 gave 0.2508  $\text{CO}_2$  and 0.0197  $\text{H}_2\text{O}$ .  $\text{C}=34.30$ ;  $\text{H}=1.09$ .

2020 .. 40.6 c.c.  $\text{N}_2$  at  $18^{\circ}$  and 752 mm.  $\text{N}=23.39$ .

2515 .. 0.2112  $\text{AgCl}$ .  $\text{Cl}=14.46$ .

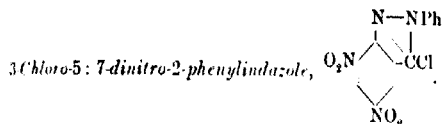
$\text{C}_7\text{H}_4\text{O}_4\text{N}_2\text{Cl}$  requires  $\text{C}=34.66$ ;  $\text{H}=1.19$ ;  $\text{N}=23.09$ ;  $\text{Cl}=14.64$  per cent.



5:7-Dinitro-3-keto-1:3-dihydroindazole was heated under pressure with 10 parts by weight of phosphoryl chloride for ten hours at  $160-180^{\circ}$ . The product was isolated in the same manner as in the previous preparation, and separated from glacial acetic acid in microscopic, white twinned needles, which melted at  $190.5^{\circ}$ :

1955 gave 11.8 c.c.  $\text{N}_2$  at  $18^{\circ}$  and 740 mm.  $\text{N}=12.47$ .

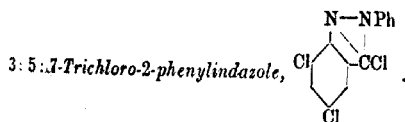
$\text{C}_7\text{H}_5\text{N}_2\text{Cl}_3$  requires  $\text{N}=12.64$  per cent.



After a sealed tube containing a mixture of 5:7-dinitro-3-keto-1:3-dihydroindazole (3 grams) and phosphoryl chloride (3 grams) had been heated for four hours at  $120-140^{\circ}$ , and cooled, it was found that the above chloroindazole derivative had crystallized. After separation from the liquor, and recrystallization from glacial acetic acid, somewhat indefinite small, greenish-yellow needles were obtained:

2000 gave 30.7 c.c.  $\text{N}_2$  at  $17^{\circ}$  and 725 mm.  $\text{N}=17.3$ .

$\text{C}_{13}\text{H}_7\text{O}_4\text{N}_4\text{Cl}$  requires  $\text{N}=17.6$  per cent.



5:7-Dinitro-3-keto-1-phenyl-1:3-dihydroindazole (5 grams) was heated with phosphoryl chloride (40 grams) for fourteen hours



under pressure at 160—170°. The product, isolated in the same manner as in the previous cases, separated from glacial acetic acid in silky, yellow needles, which melted at 208—210°.

0.1779 gave 13.8 c.c.  $N_2$  at 18.5° and 754 mm.  $N = 9.66$ .

0.3783 " 0.5429 AgCl.  $Cl = 35.53$ .

$C_{15}H_{11}N_2Cl_2$  requires  $N = 9.41$ ;  $Cl = 35.79$  per cent.

*Action of Phosphoryl Chloride on 2:4:2':4'-Tetranitro-4,4'-dicarbomethoxytetraphenylhydrazine.*

A mixture of the hydrazine derivative (3 grams) with phosphoryl chloride (40 grams) was heated for ten hours under pressure 170—180°. The product of the reaction could not be crystallized from the ordinary solvents, and was therefore purified by digestion with sodium hydroxide solution and reprecipitation from a filtered solution:

0.1815 gave 0.3572  $CO_2$  and 0.0436  $H_2O$ .  $C = 53.67$ ;  $H = 2.84$ .

0.1672 " 11.0 c.c.  $N_2$  at 20° and 731 mm.  $N = 7.4$ .

$C_{26}H_{16}O_8N_4Cl_2$  requires  $C = 53.51$ ;  $H = 2.74$ ;  $N = 9.90$  per cent.

$C_{26}H_{16}O_8N_4Cl_2$  "  $C = 55.51$ ;  $H = 2.84$ ;  $N = 4.99$  " " "

The product was therefore a mixture of two acids, derived from the original ester by hydrolysis and replacement of respectively two and four of its nitro-groups by chlorine. The incomplete nature of the reaction was probably due to the high molecular weight and sparing solubility of the hydrazine derivative.

This result is of value, since it shows that the pyrazole ring is not the predisposing cause of the mobility of the nitro-groups in the previous instances, although this mobility is specially noticeable in the naphthalene series (see the introduction), and Fraude has shown (*Annalen*, 1912, 389, 313) that 6-hydroxyindoline is comparable in its reactions with  $\beta$ -naphthol.

THE UNIVERSITY,  
SHEFFIELD.

CCLV.—*The Alkaloids of Quebracho Bark. Part I.*  
*The Constitution of Aspidospermine.*

By ARTHUR JAMES EWINS.

ASPIDOSPERMINE,  $C_{22}H_{33}O_2N_2$ , is the most readily obtained of the alkaloids of quebracho bark. It was first isolated by Fraude (*Bull.* 1878, 11, 2189) from the bark of *Aspidosperma Quebracho*, "quebracho blanco" of the Argentine, where it at one time found employment in the treatment of fever. A further investigation

alkaloids of this bark was carried out by Hesse (*Annalen*, 1882, 2, 249), who claimed to have isolated no less than six different, closely related bases. Of these, however, only two, namely, aspidospermine and quebrachine, may be said to have been well characterised, and of these the latter has recently been shown to be identical with yohimbine (Fourneau and Page, *Bull. Sci. Pharmacol.*, 1914, 21, 7).<sup>\*</sup> According to Hesse, quebrachine only occurs in some specimens of the bark, and in those examined by the present author, at most only traces of this alkaloid have been found. The present paper is concerned mainly with some results obtained in experiments on the constitution of aspidospermine. At the same time the author has not so far been able to confirm the existence of the various bases described by Hesse with the exception of aspidospermine and quebrachine. Further, Hesse employed only dilute sulphuric acid for the extraction of the alkaloids from the bark, and under these conditions, as is shown by the experiments recorded in this paper, aspidospermine is hydrolysed, giving rise to a new base, the properties of which make it appear possible that the bases aspidosamine and hypoquebrachine described by Hesse may have been impure forms of this decomposition product, aspidospermine.

It may be mentioned, however, that in the course of the present work two new well-defined crystalline alkaloids were obtained in small quantity. One, characterised by its sparing solubility in water and by its failure to give colour reactions with oxidising agents, crystallised from ethyl acetate in well-formed octahedra melting at 176–177°. The other is very sparingly soluble in water, and crystallised from light petroleum in stout prisms melting at 149–150°. The latter base gives colour reactions which resemble those given by the base obtained by the hydrolysis of aspidospermine, but are less intense. It is hoped that these bases will form the subject of a future investigation.

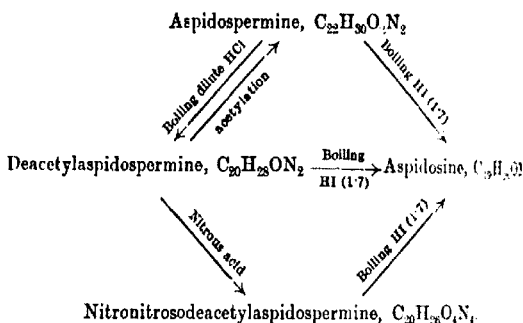
Aspidospermine is a feeble base, which does not yield crystalline

By fractional precipitation of a portion of the crude alkaloid as tartrate a small quantity of a crystalline salt was obtained from which a crystalline base melting at 225–226° was isolated. This base corresponded in general with that described by Hesse as quebrachine, and the recent statement by Fourneau and Page (1914), that the latter base is identical with yohimbine, was confirmed by the melting observations. A specimen of yohimbine (for which I am indebted to Dr. Berger) melted at 236°, and a mixture of equal parts of the two bases melted at the same temperature. Both bases melt to a red liquid and sublime at 210/5 or 6 mm., forming clusters of prismatic needles. Further, Berger and Field have found (*private communication*) that yohimbine gives a characteristic sulphonic acid derivative. The formation of this acid from the base (quebrachine) mentioned above was carried out, and its identity with that obtained from yohimbine readily established.

salts. It is levorotatory. It does not react with methyl iodide except after prolonged heating at  $100^{\circ}$ , and then yields a number of products which have not yet been investigated. Aspidospermine contains one methoxyl group, and does not contain an *benzoyl* group, but has an acetyl group attached to one nitrogen atom. This is shown by the following facts.

The hydriodic acid solution obtained after treating aspidospermine according to Zeisel's method yielded a new base, *deacetylaspidospermine*,  $C_{20}H_{28}ON_2$ . This base therefore differed in composition from aspidospermine by the complex  $C_2H_4O$ , of which the hydrolysis of one methoxyl group accounts for  $CH_2$ . The residual  $C_2H_4O$  points to the presence, in aspidospermine, of an acetyl group, which from the constitution of the base, must be attached to a nitrogen atom. The presence of an acetyl group was confirmed by the following results.

Aspidospermine on hydrolysis with boiling dilute hydrochloric acid gives a new crystalline base, *deacetylaspidospermine*,  $C_{20}H_{28}ON_2$ , which is readily reconverted into aspidospermine by acetylation. The new base on boiling with concentrated hydrochloric acid (D 1.7) as would be expected yields aspidosine, the relationship of these bases being shown as follows:



Deacetylaspidospermine forms a characteristic, sparingly soluble crystalline *dihydriodide*; the corresponding *hydrochloride* and *hydrobromide* are very readily soluble, and have not been obtained crystalline. It combines with methyl iodide, forming a crystalline derivative having the composition  $C_{20}H_{28}ON_2 \cdot 2CH_3I$ . It yields a monoacetyl derivative (aspidospermine) and a crystalline *benzoyl* derivative. It reacts with nitrous acid, and under small conditions yields a crystalline derivative, which appears to be a nitronitroso-compound. Deacetylaspidospermine thus appears to be a secondary tertiary base. The formation of a nitronitroso-derivative

together with the colour reactions of the base, probably due to the presence in the molecule of a reduced quinoline ring. On boiling with hydriodic acid, nitronitrosodeacetylaspidospermine yields aspidosine. Deacetylaspidospermine is optically active, but of opposite sign (dextrorotatory) to that of aspido-spermine.

Aspidosine is a crystalline levorotatory base, which, like deacetylaspido-spermine, gives a characteristic, sparingly soluble, crystalline hydrochloride of the composition  $C_{19}H_{25}ON_2 \cdot HCl$ . It is less basic than deacetylaspido-spermine, probably owing to the presence of a phenolic hydroxyl group. Probably also for this reason the base is somewhat unstable in solution.

On oxidation with chromic acid, aspido-spermine yields a new crystalline base, which forms a sparingly soluble hydrochloride. Owing to want of material the base has not yet been fully investigated. It gives none of the colour reactions characteristic of aspido-spermine and its immediate derivatives.

#### EXPERIMENTAL.

##### *Preparation of Aspido-spermine.*

The finely ground bark was completely extracted with hot alcohol (about 95 per cent.), and the alcohol removed by distillation. The coloured, viscous residue was extracted with a 20 per cent. solution of acetic acid until the extracts gave only very feeble colour reactions. The extract was diluted, which caused the precipitation of a certain amount of resin, and, without filtration, mixed with a saturated aqueous solution of normal lead acetate, until the filtrate no longer gave a precipitate either on dilution or addition of lead acetate. The precipitate was collected, the lead removed from the filtrate as sulphide, and the solution made alkaline with ammonium hydroxide. A voluminous precipitate was obtained, which was collected and dried. The filtrate still contained some alkaloid in solution, which was readily removed by reaction with chloroform. The residue obtained on distilling off the chloroform was added to the crude alkaloid first precipitated. The mixture of bases so obtained was dissolved in a small amount of absolute alcohol, and on keeping, aspido-spermine crystallised out. It was collected and purified by recrystallisation from methyl alcohol, or, for analysis, by sublimation in a vacuum.

According to Hesse (*loc. cit.*) quebrachine is present crystallises as aspido-spermine under conditions similar to those described above. In the present investigation, however, quebrachine was not found to be present.

The alcoholic mother liquors still contained a very considerable

amount of crude alkaloid. Attempts have been made to work out a satisfactory method of separation of the bases present in this material, but so far without very much success. Evidence has been obtained, however, of the presence of at least two hitherto undescribed crystalline bases, but the amounts so far obtained are too small to permit of further investigation.

The separation of aspidospermine from the crude alkaloids by the method described above is by no means sharp. As stated, however, aspidospermine on hydrolysis with dilute mineral acids gives a new base, deacetylaspidospermine, which can be distilled under greatly diminished pressure, and is very readily soluble in light petroleum.

The crude alkaloids obtained from the alcoholic mother liquor after separation of aspidospermine were therefore boiled with 20 per cent. hydrochloric acid for two hours. The solution was then filtered and the filtrate made alkaline with ammonium hydroxide. The precipitated bases were collected and dried, and both the residue material and the alkaline filtrate then completely extracted with light petroleum.

The extracts were combined, the solvent removed by distillation and the residue distilled under 1—2 mm. pressure. The distillate which collected between 210° and 220°, was dissolved in hot dry acetone, and on cooling crystals of almost pure deacetylaspidospermine melting at 109° were obtained. The increased amount of base isolated by this procedure corresponded in some instances with as much as 40 per cent. of the amount of aspidospermine originally obtained.

The amount of aspidospermine present in quebracho bark appears to vary considerably. From one batch of bark (50 kilos.) a yield of only 0.06 per cent. of aspidospermine was obtained, whilst from smaller batches yields up to 0.2 per cent. were obtained. The total alkaloid of the bark varies considerably with age. According to Hesse (*loc. cit.*), the young bark contains up to 1.4 per cent. alkaloid, whilst old bark may contain as little as 0.3 per cent.

*Aspidospermine*,  $C_{22}H_{30}O_2N_2$ , crystallises from alcohol or light petroleum in needles melting at 208°. It sublimes under diminished pressure at about 180°, and can be distilled under 1 mm. pressure at about 220°. It is fairly readily soluble in most organic solvents, but almost insoluble in water. It is precipitated by acids from acid solution as a white, amorphous solid, which becomes crystalline after keeping for a few minutes. Aspidospermine is only feebly basic, and does not form crystalline salts. It dissolves in concentrated sulphuric acid, forming a colourless solution, from which it may be recovered unchanged after prolonged keeping.

addition of a crystal of potassium dichromate to this solution gives a brown coloration, which becomes olive-green after some time. On heating with perchloric acid, aspidospermine gives a rose-red color.

Aspidospermine is levorotatory. Determinations of its specific rotatory power gave the following results:

(1) in alcoholic solution at  $18^{\circ}$ ,  $\alpha_D -1.79^{\circ}$ ,  $c=1.81$ ,  $l=1$  dm.;  $[\alpha]_D -99^{\circ}$ .

(2) in chloroform solution at  $18^{\circ}$ ,  $\alpha_D -1.68^{\circ}$ ,  $c=1.81$ ,  $l=1$  dm.;  $[\alpha]_D -93^{\circ}$ .

The corresponding values obtained by Hesse (*loc. cit.*) were  $+10.2^{\circ}$  and  $-83.6^{\circ}$  respectively.

The formula  $C_{22}H_{30}O_2N_2$ , originally due to Fraude and later confirmed by Hesse, was confirmed by analysis (Found, C=74.2; H=8.6; N=8.3. Calc., C=74.5; H=8.4; N=8.0 per cent.), and further by the constitution of the bases derived from it, as will be seen below.

A determination of the molecular weight by Barger's microscopic method (T., 1904, 85, 286) gave the following result:

0.66 in 0.549 pyridine = 0.25 mole. M.W. = 408.

$C_{22}H_{30}O_2N_2$  requires M.W. = 356.

A determination of the methoxyl groups present in the base was made according to Perkin's modification of Zeisel's method:

0.131 gave 0.1406 AgI. OMe = 8.7.

$C_{22}H_{30}O_2N_2$  requires OMe = 8.7 per cent.

Aspidospermine therefore contains one methoxy-group. Further heating with hydriodic acid up to  $300^{\circ}$  or rather higher according to Herzog and Meyer's method showed that the base contained no methyl group.

#### *The Action of Boiling Hydriodic Acid on Aspidospermine.*

##### *Formation of a New Base, Aspidosine, $C_{19}H_{28}ON_2$ .*

It was observed that, after treatment of aspidospermine with hydriodic acid for the determination of the methoxyl group, the residue which remained after removal of the bulk of the hydriodic acid by distillation consisted of needles with a metallic lustre, obviously the periodide of a base. The pure base was obtained in small quantities as follows. One gram of aspidospermine was boiled one and a-half hours under reflux with 20 c.c. of hydriodic acid (17). At the end of this time the excess of hydriodic acid was removed by distillation under diminished pressure, the residue suspended in water and decolorised by sulphur dioxide. The resulting solution was filtered from a small amount of flocculent material,

and made alkaline by the addition of ammonia. The amorphous precipitate rapidly became crystalline, and was collected and dried. The product was almost pure, and weighed 0.81 gram.

For purification the base was recrystallised from alcohol or benzene, when it was obtained in well-formed, rectangular plates, which melted at  $244\text{--}245^\circ$  after sintering from about  $220^\circ$ . Repeated recrystallisation failed to effect any change of melting point:

0.1260 gave 0.3526  $\text{CO}_2$  and 0.0994  $\text{H}_2\text{O}$ .  $\text{C}=76.3$ ;  $\text{H}=8.4$   
0.1634 " 13.2 c.c.  $\text{N}_2$  (moist) at  $20^\circ$  and 763 mm.  $\text{N}=9.4$

$\text{C}_{19}\text{H}_{26}\text{ON}_2$  requires  $\text{C}=76.5$ ;  $\text{H}=8.7$ ;  $\text{N}=9.4$  per cent.

*Aspidosine* is fairly readily soluble in alcohol, ethyl acetate, benzene, and xylene, very sparingly so in chloroform or light petroleum, and almost insoluble in water. Its solutions in organic solvents become coloured on keeping, and the base itself was invariably dark brown or black. For these reasons accurate determinations of the molecular weight of the base could not be made. It is levorotatory, with about  $[\alpha]_D -16^\circ$  in alcoholic solution. In the presence of dilute acid the base gradually dissolves, forming a greenish-blue solution.

*Aspidosine* gives very intense colour reactions. It dissolves in concentrated sulphuric acid, forming a pale rose-red solution. Addition of oxidising agents, such as potassium dichromate, potassium permanganate, or nitrous acid produces a reddish-violet coloration. A trace of nitric acid added to a few drops of the sulphuric acid solution gives a deep orange-red colour. Crystals of *aspidosine* heated with ferric chloride are coloured greenish-blue, gradually changing to reddish-brown. In dilute acid solution the base gives with ferric chloride a reddish-brown colour, which passes through brown to purple to deep red.

*Aspidosine Hydriodide*,  $\text{C}_{19}\text{H}_{26}\text{ON}_2\cdot\text{HI}$ .—This salt was obtained during the preparation of the base described above. To the solution which has been treated with sulphur dioxide, ammonia is added drop by drop, a crystalline solid separates even while the solution remains distinctly acid. This proved to be the hydriodide of *aspidosine*, the free base being obtained from it on further treatment with ammonia. The salt is very sparingly soluble in cold, but very readily so in hot water, from which it crystallises on cooling in regular octahedra and cubes. Its melting point is above  $280^\circ$ . The salt is anhydrous:

0.1048 gave 0.0588  $\text{AgI}$ .  $\text{I}=30.3$ .

$\text{C}_{19}\text{H}_{26}\text{ON}_2\cdot\text{HI}$  requires  $\text{I}=29.8$  per cent.

*The Action of Dilute Hydrochloric Acid on Aspidospermine.  
Formation of Deacetylaspidospermine,  $C_{20}H_{28}ON_2$ .*

One gram of aspidospermine was heated for three hours at  $100^\circ$  in 10 c.c. of 10 per cent. aqueous hydrochloric acid. The resulting solution was rendered alkaline when an amorphous base was precipitated, which on keeping for a short time became crystalline. It was collected and recrystallised from dilute acetone, when it formed long, prismatic needles, melting at  $110-111^\circ$ :

0.1356 gave 0.3803  $CO_2$  and 0.1092  $H_2O$ .  $C=76.5$ ;  $H=8.9$ .

0.1464 .. 11.4 c.c.  $N_2$  (moist) at  $10^\circ$  and 767 mm.  $N=9.36$ .

0.1562 .. 0.1362 AgI.  $OMe=9.7$ .

$H_2ON_2$  requires  $C=76.9$ ;  $H=9.0$ ;  $N=9.0$ ;  $OMe=9.9$  per cent.

Deacetylaspidospermine is readily soluble in most organic solvents, but very sparingly so in water. It distils unchanged at about  $100^\circ$  under 1-2 mm. pressure. It dissolves in sulphuric acid to a colourless solution, which on the addition of a drop of nitric acid gives a violet, or of potassium dichromate a deep brownish-purple colour. With ferric chloride a magenta colour is produced. With water oxidising agents, such as mercuric acetate, a rose-red colour is obtained, which slowly changes to violet.

Deacetylaspidospermine is feebly dextrorotatory; a 2.5 per cent. solution in absolute alcohol has  $[\alpha]_D +2.8^\circ$ .

Deacetylaspidospermine hydriodide is obtained when deacetylaspidospermine is dissolved in a small quantity of hot dilute hydriodic acid. On cooling the hydriodide separates in stout, rectangular prisms, melting at about  $243^\circ$  after sintering from  $220^\circ$ . The salt is very sparingly soluble in cold, but fairly readily in hot water, or alcohol:

0.1134 gave 0.0920 AgI.  $I=43.8$ .

$C_{20}H_{28}ON_2 \cdot 2HI$  requires  $I=44.7$  per cent.

Benzoyldeacetylaspidospermine is obtained by benzoylating the base either by Einhorn's method in pyridine solution or by heating at  $100^\circ$  for one hour with benzoic anhydride. It crystallises from dilute alcohol in stout rhombs melting at  $186-187^\circ$ :

0.1017 gave 0.2904  $CO_2$  and 0.0720  $H_2O$ .  $C=77.9$ ;  $H=7.9$ .

0.1246 .. 7.5 c.c.  $N_2$  (moist) at  $19^\circ$  and 764 mm.  $N=7.0$ .

$C_{27}H_{32}O_2N_2$  requires  $C=77.9$ ;  $H=7.7$ ;  $N=6.7$  per cent.

If deacetylaspidospermine is dissolved in a small quantity of methyl iodide, the solution warmed for a few moments and then allowed to remain, a crystalline solid separates, which, when recrystallised from methyl alcohol, forms well-defined octahedra melting at  $176-177^\circ$ . It has the composition  $C_{20}H_{28}ON_2 \cdot 2CH_3I$ :



0.1046 gave 0.0804 AgI.  $I = 41.5$ .

$C_{20}H_{22}ON_2 \cdot 2CH_3I$  requires  $I = 42.6$  per cent.

*Formation of Aspidospermine by Acetylation of Deacetylaspidospermine.*

That deacetylaspidospermine is derived from aspidospermine the removal of an acetyl group is further confirmed by the following experiment, in which aspidospermine was formed by acetylation of deacetylaspidospermine. 0.2 Gram of deacetylaspidospermine dissolved in 1 c.c. of acetic anhydride, one drop of sulphuric acid added and the mixture boiled for one minute. The solution cooled, diluted with water, and rendered alkaline with ammonium hydroxide. The precipitated amorphous base was collected and crystallised from methyl alcohol. It separated in needles melting at  $206-207^\circ$ , and when mixed with an equal weight of aspidospermine showed no depression of melting point. In all other respects also it was identical with aspidospermine. The yield was practically quantitative.

*Action of Nitrous Acid on Deacetylaspidospermine: Formation of a Nitronitroso-derivative (1).*

If deacetylaspidospermine is dissolved in dilute hydrochloric acid and treated with sodium nitrite solution a crystalline solid separates, which melts indefinitely at about  $160-170^\circ$ , and on recrystallisation from a mixture of pyridine and alcohol gives a product melting at  $220-230^\circ$  after sintering from about  $200^\circ$ . The substance is obviously a mixture; it contains chlorine, and attempts to obtain a pure compound were unsuccessful. If the reaction is carried out in the presence of concentrated hydrochloric acid a deep magenta solution is obtained, from which no crystalline product could be isolated. If, however, the reaction is carried out in acetic acid solution a pure substance is obtained.

0.5 Gram of deacetylaspidospermine was dissolved in 5 c.c. of 10 per cent. solution of acetic acid. To the cooled solution saturated aqueous sodium nitrite solution was added drop by drop until the separation of a crystalline solid appeared to be complete. The solution was allowed to remain for about an hour, when the crystalline solid was collected, washed with water, and recrystallised from dilute acetone, from which it separated in pale yellow prisms, melting and decomposing at  $155-156^\circ$ . Recrystallisation from a mixture of pyridine and alcohol gave a similar product, having the same melting point:

1179 gave 0.2668 CO<sub>2</sub> and 0.0758 H<sub>2</sub>O. C=61.7; H=7.1.  
 1182 " 14.6 c.c. N<sub>2</sub> (moist) at 20° and 753 mm. N=14.1.  
 1194 " 0.1084 AgI. OMe=8.0.  
 C<sub>22</sub>H<sub>32</sub>O<sub>4</sub>N<sub>4</sub> requires C=62.2; H=6.7; N=14.5;  
 OMe=8.0 per cent.

Analysis of this product gave some trouble, since it was difficult to take extraordinary precautions to bring about complete reduction of the easily liberated nitric oxide.

The results appear to indicate that the substance is in all probability a nitronitrosodeacetylaspidospermine, and its formation points to the presence in the molecule of a reduced quinone nucleus. The substance undergoes decomposition by boiling in alcohol, but the isolation of the corresponding nitro-derivative has not so far been accomplished. In the presence of acids more rapid decomposition appears to take place.

Nitronitrosodeacetylaspidospermine (I) forms pale yellow prisms, melting and decomposing at 155–156°. It is very readily soluble in acetone or pyridine, less readily so in alcohol, and very sparingly in water. Its aqueous solution reacts faintly acid. When diluted in concentrated sulphuric acid or warmed with dilute mineral acids a brilliant reddish-purple solution is produced. With concentrated sulphuric acid it gives a dark green solution, which on cooling becomes deep red. With ferric chloride solution no colour is produced.

Boiling hydriodic acid (D 1.7) converts nitronitrosodeacetylaspidospermine into aspidosine.

#### *Oxidation of Aspidospermine with Chromic Acid.*

Two grams of aspidospermine were dissolved in 40 c.c. of dilute sulphuric acid (25 per cent. by weight). Three grams of chromic acid were gradually added in small quantities to the boiling solution, and the mixture was then boiled for five hours. The resulting solution was treated with hot saturated barium hydroxide solution until distinctly alkaline. The hot solution was filtered under pressure, the precipitate repeatedly extracted with boiling water until the extracts no longer gave alkaloidal reactions, and the combined filtrates were completely freed from sulphuric acid and chromium. The aqueous liquid was then concentrated to small bulk, made faintly acid towards Congo-red with hydrochloric acid, and further concentrated until crystallisation commenced. The solution was set aside, and after some time the crystalline product was filtered and recrystallised from absolute alcohol. The product was found to be the hydrochloride of a base which was set free by

ammonia and crystallised from ethyl acetate in stout prisms melting at 192–193°. The base is very sparingly soluble in water, but fairly readily so in alcohol, ethyl acetate, or chloroform. It gives very marked reactions with alkaloidal reagents, but gives none of the colour reactions characteristic of aspidospermine or its derivatives already described. The yield is only about 5 per cent of the weight of aspidospermine employed, and on this account the investigation of the base has not so far been possible.

The hydrochloride forms plates which melt at 286–287° and are sparingly soluble in water or in cold alcohol:

0.0956 gave 0.2104  $\text{CO}_2$  and 0.0706  $\text{H}_2\text{O}$ .  $\text{C}=60.0$ ;  $\text{H}=8.3$ .

0.1322 „ 0.0638  $\text{AgCl}$ .  $\text{Cl}=11.8$ .

$\text{C}_{15}\text{H}_{24}\text{O}_2\text{N}_2\cdot\text{HCl}$  requires  $\text{C}=59.9$ ;  $\text{H}=8.3$ ;  $\text{Cl}=11.8$  per cent.

From these results the most probable formula for the base would appear to be  $\text{C}_{15}\text{H}_{24}\text{O}_2\text{N}_2$ , but this cannot be satisfactorily established with any degree of certainty at present.

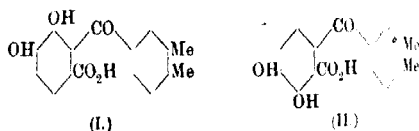
WELLCOME PHYSIOLOGICAL RESEARCH LABORATORIES,  
HERNE HILL, S. E.

## CCLVI.—Some Homologues of Alizarin.

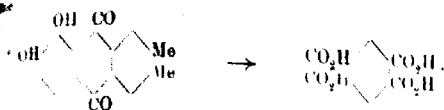
By HARRY BRADBURY and CHARLES WEIZMANN

BENTLEY and Weizmann (T., 1908, 93, 435) have shown that hemipinic anhydride condenses with veratrole and with trimethyl ether, in the former case the normal benzoylbenzoic acid is formed, but in the latter one methoxy-group is displaced by hydroxyl, the condensation in both cases being affected by the use of aluminium chloride. The object of the present work was to investigate the condensations of hemipinic anhydride with 4-methoxyphthalic anhydride with *o*-xylene, and the results were quite analogous to those just mentioned, the methoxy-group being also displaced by hydroxyl.

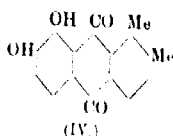
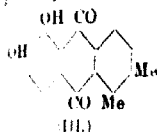
The condensation of hemipinic anhydride with *o*-xylene furnished a dihydroxy-2-xyloylbenzoic acid, which, as it gave dimethylalizarins on heating with sulphuric and boric acids, has the constitution I or II:



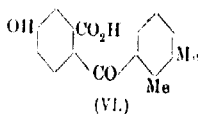
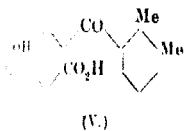
constitution of one of the two dimethylalizarins (melting at higher temperature) was determined by oxidation with potassium permanganate in alkaline solution, when pyromellitic acid was isolated. This could only have been formed according to the



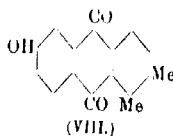
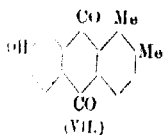
constitution of the other dimethylalizarin must be either IV, according as the original acid has the constitution I or II respectively:



For lack of material it has not yet been possible to decide this. The condensation of 4-methoxyphthalic anhydride with *o*-xylene was similarly. Two hydroxyxyloxybenzoic acids were obtained, respectively at 228° and 184°. The former, on fusion with calcium hydroxide, gave *m*-hydroxybenzoic acid, and when condensed in the usual way gave only one hydroxydimethylantracene, the formation of which points to the acid having the constitution V or VI:



the quinone VII or VIII:



#### EXPERIMENTAL.

##### *Dihydroxy-2-xyloxybenzoic Acid.*

Grams of hemipinic anhydride were dissolved in 50 grams of water, and 15 grams of aluminium chloride gradually added. The mixture was then heated on the steam-bath for six hours.

hours, when it was poured into ice and water and steam in through to remove the excess of *o*-xylene. When collected and purified by solution in ammonia and precipitation with hydrochloric acid. The product from which no crystals could be obtained crystallized from acetic acid in small crystals melting at 238°:

0.1242 gave 0.3039 CO<sub>2</sub> and 0.0522 H<sub>2</sub>O. C=66.73; H=4.90  
C<sub>16</sub>H<sub>14</sub>O<sub>3</sub> requires C=67.13; H=4.90 per cent

#### *Dimethylalizarins.*

The above acid was heated with sulphuric acid together with a small amount of anhydrous boric acid for a short time and the liquid after cooling was poured into ice and water. The dimethylalizarins separated as an orange-yellow powder and were separated by making use of their solubility in acids. The dimethylalizarin melting at 198° was readily soluble in water; that melting at 276° was sparingly soluble; each crystallized in orange-yellow needles, and resembled ordinary alizarin in its properties. The compounds readily dissolved in sodium hydroxide to give a deep purple solution, which dyed mordanted cotton in various shades being obtained according to the mordant used.

The substance melting at 276° was analysed:

0.0682 gave 0.1780 CO<sub>2</sub> and 0.0266 H<sub>2</sub>O. C=71.20; H=4.47  
C<sub>16</sub>H<sub>12</sub>O<sub>4</sub> requires C=71.64; H=4.47 per cent

The dimethylalizarin melting at 276° was oxidized with potassium permanganate in alkaline solution, and after removing excess of permanganate the filtered liquid was evaporated to dryness and the residue extracted with alcohol. On evaporation of the filtered extract and acidifying, pyromellitic acid was obtained.

#### *Hydroxy-2-xyloylbenzoic Acids.*

The condensation of 4-methoxyphthalic anhydride and xylose was carried out in an exactly similar manner to that employed in the preparation of the dihydroxy-2-xyloylbenzoic acids. The product, after being purified by dissolving in ammonia and precipitation by hydrochloric acid, was boiled with benzene. Very little appeared to pass into solution, and the residue after filtration apparently consisted of only one acid. This was crystallized from acetic acid, in which it was fairly readily soluble, and the crystals on concentration deposited small crystals melting at 227°. The fusion of this acid with potassium hydroxide was carried out as follows: Five grams were gradually added to 15 grams of potassium hydroxide, and the mixture was heated at 250°.

three hours. The cooled mass was dissolved in boiling water, the solution acidified with dilute sulphuric acid. On cooling and crystallised out, and which, when recrystallised from hot water, melted at  $200^{\circ}$  and was identified as *m*-hydroxybenzoic acid. The ether from the above acid was extracted several times with ether, and after evaporating the ether a residue remained, but *m*-hydroxybenzoic acid has not yet been isolated in a pure form.

The benzene solution mentioned above was evaporated to a thick, and crystals were obtained which, after further crystallisation from benzene, melted at  $184^{\circ}$ . The amount, however, was an exceedingly small proportion of the total yield of acid.

#### *Hydroxydimethylantraquinone.*

The acid melting at  $228^{\circ}$  was heated with sulphuric and boric acid and on pouring the mixture into water a pale green powder obtained. This was collected and crystallised twice from water, yielding small, pale green needles, melting at  $210^{\circ}$ . No quinone was detected in the product:

0.022 gave 0.4066  $\text{CO}_2$  and 0.0630  $\text{H}_2\text{O}$ .  $\text{C} = 75.86$ ;  $\text{H} = 4.78$ .

$\text{C}_{16}\text{H}_{12}\text{O}_3$  requires  $\text{C} = 76.19$ ;  $\text{H} = 4.77$  per cent.

#### *Preparation of 4-Methoxyphthalic Acid.*

In the first experiments 4-methoxyphthalic acid was prepared by Reimer and Weizmann's method (*loc. cit.*). This was found, however, to give a comparatively poor yield, and the following method was devised. 4-Hydroxyphthalic acid (1 mol.) was dissolved in water, and methyl sulphate (4 mols.) and anhydrous potassium carbonate (4 mols.) were added in this order. The mixture was heated in an oil-bath for three hours at  $135$ – $140^{\circ}$ , and then water was added to the cooled product, and the xylene separated from the aqueous portion. The latter was extracted several times with ether, and the ethereal extract added to the water layer. The ether was removed by distillation and the xylene removed by a current of steam. The oil remaining was dissolved in ether, the solution dried and evaporated, and the residue distilled under diminished pressure. The yield of methyl 4-methoxyphthalate varied from 80 to 90 per cent., depending on the rate of the passage of steam in which it is slightly volatile. The ester was hydrolyzed in the usual way by means of a solution of potassium hydroxide in alcohol, and the acid converted into anhydride.

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CCLVII.—*The Dissociation Pressures of the Alkali Bicarbonates. Part II. Potassium, Rubidium and Caesium Hydrogen Carbonates.*

By ROBERT MARTIN CAVEN and HENRY JULIUS SANDERSON.

In a former paper (T., 1911, **99**, 1359) we recorded the results of our study of the thermal dissociation of sodium hydrogen carbonate, and showed that sodium carbonate monohydrate was formed from the bicarbonate within the temperature limits of our experiments. It was stated, however, by Hermann (Z. phys. Chem., 1842, **26**, 312) that the sesquicarbonate,  $\text{Na}_2\text{H}(\text{CO}_3)_3$ , is formed when the hydrogen carbonate is heated to 200°. This result was denied by Lescœur (Ann. Chim. Phys., 1892, [vi], **25**, 42), and we determined to establish the simpler manner of dissociation of the hydrogen carbonate under the conditions of our experiment by the direct estimation of the proportion between water and carbon dioxide in the gaseous phase.

For this purpose a glass reservoir of 50 c.c. capacity was fitted on the one side through a tap to the tube leading from the flask containing the heated bicarbonate, and was connected on the other side with calcium chloride and soda-lime absorption tubes. When the reservoir and absorption tubes were exhausted, the flask was then heated above 100°, and the tap communicating with the flask opened so that the gaseous mixture might expand into the reservoir without aqueous condensation. After a few seconds the tap was closed again, and the water and carbon dioxide in the reservoir were carefully transferred to the absorption tubes. It was advantageous to allow some of the water to collect in the reservoir, and subsequently to remove it by slow evaporation, and an arrangement was made to carry forward the last trace of water-vapour and carbon dioxide in a stream of purified air.

The following results were obtained with sodium hydrogen carbonate:

Temperatures of thermostat	$\text{H}_2\text{O}$	$\text{CO}_2$	Molecular ratio $\text{H}_2\text{O}:\text{CO}_2$
101.5°	0.0118	0.0295	1:1.92
101.8°	0.0108	0.0259	1:1.97

These results were sufficient to show that water is not evolved to form the hydrated sesquicarbonate,  $\text{Na}_2\text{H}_2(\text{CO}_3)_3 \cdot 3\text{H}_2\text{O}$ .

hydrogen carbonate is heated under the conditions of our experiments, although they do not preclude the possibility of combination between sodium carbonate and sodium hydrogen carbonate to form an anhydrous intermediate salt such as  $\text{Na}_4\text{H}_2(\text{CO}_3)_3$ .

#### Potassium Hydrogen Carbonate.

As was mentioned in the former paper that Lescœur (*Ann. Chim. Phys.*, 1892, [vi], 25, 423\*) measured the dissociation pressure of sodium hydrogen carbonate, obtaining results much more than those obtained by us. The apparatus employed by him (*Ann. Chim. Phys.*, 1889, [vi], 16, 389) differed in principle from ours, and consisted of a barometer tube surrounded by a water jacket. The substance was contained in a small tube in the space above the mercury, and gas could be withdrawn from the space by means of a narrow open tube which passed down through the mercury. It is noteworthy that the vapour pressure of potassium hydrogen carbonate observed by Lescœur was slightly higher than ours at the lower temperatures, but very close to them at 127°, the highest temperature at which measurements were made by Lescœur. These results are shown by the dotted curve on our diagram.

In the study of the thermal dissociation of potassium hydrogen carbonate the possibility of the formation of a hydrated compound, normal carbonate and hydrogen carbonate, or of the retention of water by the normal carbonate, had first to be considered. Since the temperature of sensible dissociation of potassium hydrogen carbonate is considerably higher than that of the sodium salt, the formation of intermediate compounds containing water seemed much less likely than in the case of sodium. The analysis of the solid phase resulting from the decomposition of potassium hydrogen carbonate provided, however, direct evidence that water was retained to form such intermediate compounds. Measurements made in the manner described above yielded the following results:

Temperature (Thermobat.)	$\text{H}_2\text{O}$	$\text{CO}_2$	Molecular ratio $\text{H}_2\text{O} : \text{CO}_2$
145	0.0080	0.0253	1 : 1.28
150.2	0.0089	0.0232	1 : 1.07
151.1	0.0068	0.0164	1 : 0.98

It is shown that potassium hydrogen carbonate dissociates into normal carbonate, carbon dioxide, and water.

\*Reference was wrongly given as *Ann. Chim. phys.*, 1893, [vi], 28, 423.



The dissociation pressures of potassium hydrogen carbonate measured in the same way as those of sodium hydrogen carbonate and the results obtained are here tabulated, together with the calculated from the equation:

$$\log p = a - b/T,$$

where  $a = 10.832$  and  $b = 3420$ .

It should be remarked that at  $120^\circ$  and upwards the vapour pressure of mercury becomes appreciable, and consequently a correction has been applied to the pressure readings for these temperatures.

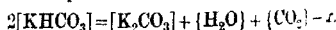
*Potassium Hydrogen Carbonate.*

Temperature.	Pressure in mm. of mercury		
	Rising.	Falling.	Calculated.
151.8	610.6	—	604
150.0	733.0	—	721
147.8	—	503.1	506
137.7	—	314.7	326
127.2	—	184.1	186
119.1	—	124.1	129
104.6	—	56.6	59.6
90.2	—	24.6	26.4
76.3	—	11.4	11.6
63.7	—	4.1	4.7
92.5	31.2	—	29.9
103.5	57.7	—	56.0
116.4	111.2	—	112
127.4	192.0	—	195
138.4	322.8	—	339
140.3	471.4	—	473
153.4	663.1	—	647
155.4	713.8	—	706

These experimental values are shown in the figure in relation to the calculated curve, together with those of sodium, rubidium, caesium. It may be pointed out that in this case the experimental values lie along the calculated curve throughout the whole range of temperature.

*Heat of Dissociation of Potassium Hydrogen Carbonate.*

From the value of the constant  $b = 3420$  the heat of dissociation of potassium hydrogen carbonate per gram-molecule of gas produced is calculated by means of the equation  $q = 2.303 RT \log p$  = 15,730 calories, since  $\log_{10} 10 = 2.30$  and  $R = 2$ . As in the case of sodium hydrogen carbonate, the heat of dissociation,  $q$ , of  $x$  gram-molecules of potassium hydrogen carbonate may be calculated from the thermal equation:



heats of formation from their elements of 1 gram-molecule sodium hydrogen carbonate and potassium carbonate are, according to de Forcrand (*Compt. rend.*, 1909, 149, 719), respectively 231,630 and 275,370 calories, whence, accepting the heats of fusion of water as steam at  $100^{\circ}$ , and of carbon dioxide to be 1 and 97,000 calories respectively,  $x = 32,830$ , instead of as calculated from our results.

*Rubidium and Cæsium Hydrogen Carbonates.*

Rubidium and cæsium\* hydrogen carbonates were prepared from normal carbonates according to de Forcrand's method (*Compt.* 1909, 149, 719) by exposing concentrated solutions of the salts to an atmosphere of carbon dioxide in a desiccator being sulphuric acid. In some earlier experiments on the dissociation pressure of rubidium hydrogen carbonate a small portion of the normal carbonate was mixed with it previous to its introduction into the reaction flask, but, owing to the very hygroscopic nature of the latter salt, it was judged better to produce an effect of it sufficient to secure the satisfactory reversal of the reaction by heating the bicarbonate in the reaction flask itself, pumping out the dissociation products. Since it had been found that potassium as well as sodium hydrogen carbonate yields dissociation products in equimolecular proportions of water-vapour and carbon dioxide, it was at first thought safe to assume that rubidium and cæsium hydrogen carbonates would behave similarly when heated; but, owing to difficulty in interpreting the experimental results to be recorded below, the composition of the gaseous products was estimated in the case of these salts also.

The determination of the dissociation pressures of rubidium and cæsium hydrogen carbonates was carried out in the apparatus already employed. Sixteen grams of the rubidium salt were heated to about  $160^{\circ}$ , and gas was repeatedly withdrawn at that temperature until successive readings after restoration of pressure were obtained. In the case of cæsium hydrogen carbonate, about 18 grams were employed, and the salt was heated to  $163^{\circ}$  until the pressure was constant after successive withdrawals of gas. Retardation of the reaction, such as was observed in the case of sodium hydrogen carbonate, which necessitated the employment of a much larger quantity of the reacting substance, did not occur with either salt. It was, however, to the lengthened heating at high temperatures, and to the fact that the temperature of the air above the sulphuric

sulphuric acid carbonate could not be purchased, but fortunately the amount of this substance was sufficient for our experiments.

acid bath was slightly lower than that of the acid thermometer and reaction flask were immersed. The mercury within the thermometer took place, and the readings might be several degrees too low. This was partly overcome by fixing the thermometer so that the mercury column was always above the level of the acid, the thus introduced being negligible. When, however, elements of mercury thread appeared in the upper part of the meter, it was necessary to reject the readings.

The following are the experimental results obtained with those calculated from the formula  $\log p = a - b/T$  for  $\text{RbHCO}_3$ ,  $a = 12.712$ ,  $b = 4300$ , and for  $\text{CsHCO}_3$ ,  $a = 12.712$ ,  $b = 6300$ .

*Rubidium Hydrogen Carbonate.*

Temperature.	Pressure in mm. of mercury.		
	Rising.	Falling.	Calculated.
160°	—	594.1	605
153.5	—	451.7	477
135.3	—	197.9	182
120.5	—	116.5	100
109.3	—	75.5	52.2
97.3	—	49.3	32.6
91.2	—	40.9	28.0
61.5	—	18.4	9.7
12.7	—	0.7	0.0
106.5	51.5	—	24.1
120.1	97.0	—	59.4
137.3	211.9	—	171
146.8	323.1	—	265
151.9	405.9	—	302
161.0	623.7	—	638
170.6	1,038.4	—	1,047
164.0	—	750.0	747
158.4	—	552.5	556
151.5	—	392.2	383
143.2	—	247.8	240
135.2	—	179.0	151
121.2	—	96.3	61.8
112.9	—	75.4	37.2
95.8	—	49.8	11.3
15.0	—	0.0	0.0
111.4	76.0	—	33.6
136.5	217.1	—	103
147.1	343.2	—	200
153.5	446.3	—	427
158.6	562.4	—	562

*Cæsium Hydrogen Carbonate.*

Pressure in mm. of mercury.

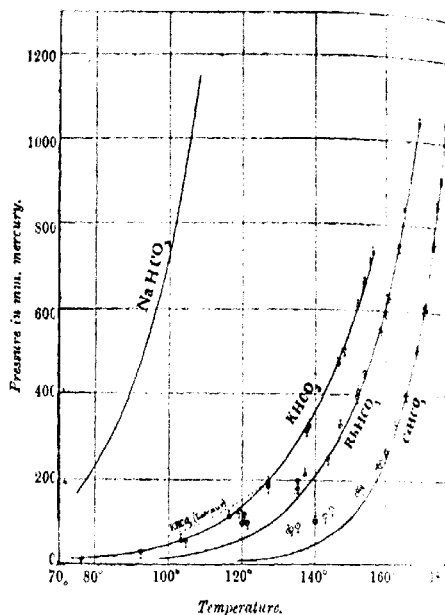
Temperature.	Rising.	Falling.	Calculated.
163.0°	322.8	—	303
160.1	—	267.0	242
153.1	—	180.0	140
142.7	—	115.9	59.6
133.6	—	81.0	27.3
116.5	—	46.5	5.7
103.8	—	28.3	1.6
89.5	—	16.3	0.4
103.0	28.8	—	1.5
117.9	47.5	—	6.5
133.1	79.3	—	24.0
140.0	100.7	—	47.4
151.6	168.9	—	124
158.1	234.8	—	207
169.9	502.1	—	507
172.2	599.7	—	601
177.0	847.1	—	851
179.8	1,029.5	—	1,038
178.1	—	915.1	921
175.4	—	755.0	759
172.7	—	614.1	624
166.1	—	399.8	382
157.8	—	241.0	202
152.4	—	183.3	132
144.5	—	130.6	69.2
135.3	—	91.5	31.6

These results differ in an important way from those obtained with potassium hydrogen carbonate. For whilst the experimental values lie along the curve throughout its whole length in the case of the potassium salt, it is only the pressures above 158° with rubidium hydrogen carbonate, and above 165° with cæsium hydrogen carbonate, that agree with the values calculated from the equation.

Discordant pressure values were obtained at the lower temperatures in the case of sodium hydrogen carbonate, but these were seen to be due to retardation, ascending values being too low, and descending values were too high. Here, however, ascending and descending values agree; they therefore appear to indicate a true equilibrium. Consequently no single curve of the type  $p = a + bT$  can be drawn to represent the experimental values obtained in the dissociation of rubidium and cæsium hydrogen carbonates, and it became necessary to investigate the cause of the anomaly.

This could best be done by the analysis of the gaseous phase, which was consequently carried out with both these salts, but in greater detail with rubidium hydrogen carbonate. About 19 grams of the latter salt, pulverised and dried over sulphuric acid in a

vacuum desiccator for several days, were heated in the reaction flask to  $120^{\circ}$  for twenty-four hours; the flask was then exhausted and any water vapour that had been evolved was drawn off through a calcium chloride tube. The delivery tube was then attached to weighed calcium chloride and soda-lime tubes, and the flask was heated to  $170^{\circ}$ . The products evolved at this temperature were passed through the absorption tubes by maintaining a reduced pressure on the further side until it was judged that a known



absorption had taken place. The flask was then exhausted and the whole of the water-vapour and carbon dioxide collected in the absorption tubes. In two successive experiments 0.0628 and 0.077 gram of water and 0.1400 and 0.1835 gram of carbon dioxide were collected; these correspond with the molecular ratios  $\text{H}_2\text{O}:\text{CO}_2$  1:0.94 and 1:0.98. Thus it was shown that water-vapour and carbon dioxide are evolved in approximately equimolecular proportions from rubidium hydrogen carbonate at  $170^{\circ}$ .

The reaction mixture was then allowed to cool somewhat, and

proportions between the two components of the gaseous phase estimated at temperatures approaching and corresponding to those at which anomalous pressure values appear on the dissociation curve. Owing to the small quantities of gas evolved in the experiments it was necessary to allow the absorption to continue over lengthened periods of time, amounting at the lower temperatures to two days; nevertheless, interesting results were obtained under parallel conditions, which are here shown:

Temperature.	H <sub>2</sub> O.	CO <sub>2</sub> .	Molecular ratio H <sub>2</sub> O : CO <sub>2</sub> .
145°	0.0197	0.0507	1 : 1.016
132°	0.0147	0.0343	1 : .937
131°	0.0053	0.0108	1 : .847
127°	0.0087	0.0164	1 : .770
125°	0.0180	0.0336	1 : .763

Before a definite interpretation could be given to the undoubted agency of carbon dioxide or excess of water-vapour in the gaseous phase at the lower temperatures it was necessary to know the ratio between the amounts of these substances remaining in the residue. To discover this ratio a fresh experiment was carried out with 1 gram of carefully dried rubidium hydrogen carbonate, which was heated in the silica flask previously employed in the experiments with sodium hydrogen carbonate, this flask being used to avoid the possibility of the absorption of carbon dioxide by the salt. In three successive experiments carried out at 123° the following molecular ratios were found: H<sub>2</sub>O : CO<sub>2</sub> = 1 : 0.731, 1 : 0.618, 1 : 0.662; but on ignition of the residue this ratio was found to be 1 : 0.995. Thus it was shown that excess of water-vapour was present in the gaseous phase at the lower temperatures is extraneous water, and is not derived from the preferential loss of water from the salt itself.

Similar experiments carried out with a small quantity of caesium hydrogen carbonate pointed to a like conclusion. At 173° and 150° the molecular ratios found were H<sub>2</sub>O : CO<sub>2</sub> = 1 : 1.009 and 1 : 1.005 respectively; at lower temperatures water-vapour was slowly evolved even after all the carbon dioxide had been exhausted.

It had been concluded that the rubidium, as well as caesium hydrogen carbonate, prepared for and employed in these experiments was pure and dry, because the loss incurred on ignition of the former salt closely agreed with theory; but it remained possible that this agreement was due to compensation, and that the product was really a mixture of rubidium normal and hydrogen carbonates, together with some water. A further experiment in which 1 gram of the salt dried as described above was heated, and all the evolved products were collected and weighed showed that it contained

0.0804 gram of water instead of 0.0614 gram, and of carbon dioxide instead of 0.1500 gram, the total loss being 0.2081 gram instead of 0.2114 gram according to theory. The anomalous pressure values obtained at the lower temperatures with rubidium and caesium hydrogen carbonates are therefore, to the following cause.

The salts employed contained a certain proportion of water carbonates, together with some water tenaciously held in spite of careful drying. This water was not present in sufficient amount, however, perceptibly to interfere with the equilibrium proportions between the water vapour and carbon dioxide evolved from the bicarbonate at high temperatures and pressures, and removal of some of the gas; as was proved by direct experiment (see p. 2758), and by the fact that successive readings were the same. When, however, the temperature was lowered and absorption took place, excess of water vapour, although small as regards absolute value, would become relatively great owing to the smallness of the total amount of gas left, and would thus become prominent in greatly increasing the observed pressures. The anomalies exist in the lower parts of the dissociation pressure curves for rubidium and caesium hydrogen carbonates are therefore almost certainly to be attributed to the exceedingly hygroscopic nature of these normal carbonates of these metals. It may here be pointed out, moreover, that the curves would tend to become too shallow on account of any small excess of water vapour present in the gas phase.

#### *Heats of Dissociation of Rubidium and Caesium Hydrogen Carbonates.*

From the equation  $q = \log_{10} R/b$ , when  $b = 4300$  and  $q = 3.6$  respectively, the heats of dissociation are calculated to be for rubidium hydrogen carbonate 19,780 cal. and for caesium hydrogen carbonate 28,980 cal.

According to de Forcrand (*Compt. rend.*, 1909, **149**, 719) the heats of formation per gram-molecule are 231,920 and 271,920 cal. for  $\text{RbHCO}_3$  and  $\text{Rb}_2\text{CO}_3$ , and 232,930 and 274,540 cal. respectively for  $\text{CsHCO}_3$  and  $\text{Cs}_2\text{CO}_3$ ; whence the heats of dissociation of two gram-molecules of  $\text{RbHCO}_3$  and  $\text{CsHCO}_3$  are calculated to be 33,800 and 36,260 cal. respectively, instead of 39,960 and 59,960 cal. derived from our results.

We are unable to offer any explanation of the discrepancy between our thermal values and those of de Forcrand. The values might be approximated by the reduction of the value of  $b$  in the equation  $\log p = a - b/T$ , which would involve a reduction

The steepness of the corresponding dissociation pressure curves, increasing steepness from potassium to caesium is well shown in the figure by the increased curvature apparent midway in the series, which is especially apparent with caesium.

It has been shown above, however, that the only cause of error which we at present recognise, that is, the departure from equimolecular proportions in the gaseous phase, would have the opposite tendency of making the curves too shallow. Consequently we cannot admit the validity of reducing the values of the constant in the two equations. On the other hand, whilst we cannot make any general criticism of the conclusions of de Forcrand, it may be pointed out that they are based on diminishing values for heats of formation of the normal carbonates from potassium caesium, namely,  $K_2CO_3 = 275,370$  cals.,  $Rb_2CO_3 = 274,900$  cals.,  $Cs_2CO_3 = 274,540$  cals.; values which we should certainly a priori consider improbable.

The results of our experiments on the dissociation pressures of alkali bicarbonates show, not only that the stabilities towards heat of these salts increase with rise of atomic weight and accompanying increase in electropositiveness of the metals, but also that ammonium hydrogen carbonate is widely separated from the other alkali salts in stability.

Thus there is furnished another example of the fact that a gradation occurs in the gradation of properties of compounds of the alkali metals at the point of transition from the short to the long periods in the periodic classification of the elements.

We desire to express our indebtedness to the Research Fund Committee of the Chemical Society for a grant which has defrayed a great part of the cost of this investigation.

UNIVERSITY COLLEGE,  
NOTTINGHAM.

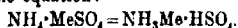
THE SIR JOHN CARR  
TECHNICAL INSTITUTE, LONDON.



CCLVIII.—*The Isomeric Transformation of Ammonium Methyl Sulphate, and of Substituted Ammonium Methyl Sulphates; the Interaction of Ammonium Hydrogen Sulphate and Methyl Sulphate.*

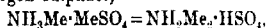
By EMIL ALPHONSE WERNER.

In a recent communication (this vol., p. 925) containing an account of the study of the decomposition by heat of the methyl sulphates of certain isocarbamides, it was pointed out that ammonium methyl sulphate can evidently undergo isomeric change when heated in accordance with the equation:

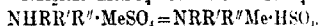
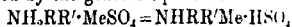


This interesting reaction, which does not appear to have been hitherto recorded, was only noticed as a qualitative change in connexion with the investigation referred to above. A more detailed study of the change has now been made, the results of which have shown that an isomeric transformation on the line above is apparently a property common to all substituted ammonium methyl sulphates, where such an interchange in the position of a hydrogen atom and a methyl group is possible.

Thus when methylammonium methyl sulphate, the simplest preparation of which from ammonia and methyl sulphate is described further on, is heated it gradually changes to the isomeric form, ammonium hydrogen sulphate,



and the further progress and limit of the isomeric transformation may be expressed by the general equations:

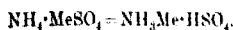


Whilst the alcohol radicles may be variants, the isomeric change appears to be restricted to the methyl sulphates, since neither ammonium ethyl sulphate nor ammonium *n*-propyl sulphate were found to undergo any isomeric change. Decomposition with formation of ammonium hydrogen sulphate and ethylene or propylene respectively was the only result of the action of heat on these two salts.

The results of a quantitative study of the extent of isomeric change with rise of temperature in the case of ammonium and methylammonium methyl sulphates are given in the tables below. The time of heating was fifteen minutes in all the experiments. A comparatively short period was chosen, as preliminary experiments showed that the velocity of the isomeric change was chiefly a function of temperature.

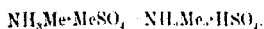
of the temperature. Since the methyl sulphates under investigation were found to be neutral in reaction, the progress of the change was readily measured by determining the acidity developed in the product at the end of each experiment.

TABLE I.\*



Temperature.	Per cent. of isomeric change.	Temperature.	Per cent. of isomeric change.
110–120°	7.0	220–230°	46.3
137–145	9.4	240–250	73.4
160	11.3	250–260	85.9
180–185	14.3	275	97.2
200–205	25.8		

TABLE II.\*



Temperature.	Per cent. of isomeric change.	Temperature.	Per cent. of isomeric change.
100–105°	2.6	210–220	34.1
135–140	6.4	230–240	50.4
150–155	7.2	250–260	81.3
170–175	8.3	275	97.8
190–200	13.9		

\* The numbers for the temperatures from 240° upwards are slightly higher than the values, on account of the small amount of secondary change referred to in experimental part.

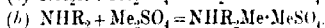
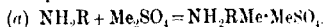
It will be seen from the above that in both cases the amount of isomeric change is small until a temperature of about 220° is reached; beyond this it proceeds rapidly, and is almost complete at 275°, and with the exception of a slightly greater amount of isomerisation for the lower temperatures in the case of ammonium methyl sulphate there is practically no difference in the general order of the change for these two salts. The influence of time on the velocity of isomeric change is small even just below 220°; thus in the case of ammonium methyl sulphate after heating for one hour at 200–205° the percentage of isomerisation was raised from 15.8 (for fifteen minutes) to 34.2, whilst with the methylammonium salt at 210–220° there was an increase from 34.1 to 46.9 per cent. at the same difference in period.

A few different types of substituted ammonium methyl sulphates have been examined, all of which apparently undergo an isomeric change, and in the case of derivatives containing more complex alkyl groups or a phenyl group this proceeds more readily than with the methyl sulphates recorded above; for example, methylpropylammonium and phenyldimethylammonium methyl sul-

phates were found to undergo isomeric change to the extent of about 35 and 48 per cent. respectively at 140°, whilst even at 100° there was a very appreciable amount of change.

It is hoped to make a systematic quantitative study of a number of different methyl sulphates as soon as opportunity permits.

As regards the mechanism of this isomeric change it is very probable that dissociation, as the first step towards a stable equilibrium, precedes the formation of the isomeric form. When ammonium methyl sulphate is heated it will dissociate into the production of methylamine and sulphuric acid rather than ammonia and the very unstable methyl hydrogen sulphate. From the union of the dissociation products the still more stable methylammonium hydrogen sulphate will be formed. This explanation is in agreement with the conditions under which the isomeric change has been shown to take place, and also with the fact that the methyl sulphates of the feeble (benzenoid) ammonium bases undergo isomerisation readily at correspondingly lower temperatures. Considered from a practical point of view, the recognition of this general isomeric change is likely to prove of some value since it appears to place in our hands a method more simple than any of those hitherto available for the preparation of many substituted methylammonium bases, more particularly on account of the ease with which the methyl sulphates may be prepared from the interaction of the amines and methyl sulphate, in accordance with the general equations:



It also explains certain discrepancies in the results which have been published hitherto with regard to the above reactions. Thus, Claesson and Lundvaal (*Ber.*, 1880, **13**, 1699) have shown that ammonia and aniline respectively react with methyl sulphate according to equation (a), they state that in the case of benzylamine and methyl sulphate the products formed are benzylammonium and dimethyldiethylammonium methyl sulphates. More recently Ullmann (*Annalen*, 1903, **327**, 104), who has examined the behaviour of aniline and a number of its ortho homologues towards methyl sulphate, has arrived at the conclusion that in the case of aromatic amines the interaction does not follow the course described by Claesson and Lundvaal (*loc. cit.*), but that for primary amines is to be represented by the general equation



for example, with aniline the products formed are stated to be aniline methyl sulphate, methylaniline, and a certain amount of dimethylaniline. The experimental conditions adopted, more especially

by Ullmann, were such that much heat was allowed to develop during the interactions, with the result that more or less isomeric change must have taken place, to which cause must be attributed the different conclusions arrived at regarding the general order of interaction. The results of experiments with several different bases, aliphatic and aromatic, have shown that if care be taken around anything more than a slight development of heat, the reactions with methyl sulphate proceed in a perfectly straightforward manner in accordance with equations (a) and (b); practically quantitative yields of the substituted ammonium methyl salts have been obtained without any trouble.

#### EXPERIMENTAL.

##### *Preparation of, and Action of Heat on, Ammonium Methyl Sulphate.*

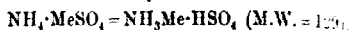
The following method of preparation was found to give a fairly good yield of the above salt in a high degree of purity. The reactant obtained after heating a mixture of 50 grams of pure methyl alcohol and 100 grams of pure sulphuric acid on the water-bath for half-an-hour was cooled and directly neutralised by addition of powdered commercial ammonium carbonate until, with occasional addition of a small quantity of water, a pasty, slightly alkaline mass was obtained; this was extracted with about 100 cc. of boiling methyl alcohol, the cold solution was poured off and any ammonium sulphate which separated, and concentrated to about half the volume by careful distillation. While hot the solution was again poured off from any substance which had settled, and on cooling it set to a mass of thin, plate-like crystals of satiny lustre. After a further recrystallisation from absolute methyl alcohol the salt was obtained quite free from even a trace of sulphate, and was almost neutral in reaction; 32 grams of pure ammonium methyl sulphate were obtained from 50 grams of methyl

\* pure salt melts at  $137^{\circ}$ , and is exceedingly hygroscopic; it is more soluble in ethyl alcohol than in methyl alcohol, hence the preference of the latter solvent for its purification.

In order to study the progress of the isomeric change, a series of test-tubes containing weighed quantities of the well-dried salt were placed in a bath of glycerol for fifteen minutes to the desired temperature; the bulb of a thermometer, passed through a loosely-stoppered cork, was kept immersed in the fused salt during each

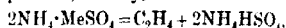
period. When slowly heated the salt may be found to melt at  $125^{\circ}$ , as a result of a gradual isomeric change.

experiment. The product was dissolved in water and titrated directly with *N*-sodium hydroxide, methyl-orange being used as indicator. On account of the very hygroscopic nature of the salt it was not advisable to attempt to weigh out a similar quantity in each experiment; from the equation:



it will be readily seen that 1.29 grams of ammonium methyl sulphate would require, after complete isomerisation, 1.29 grams of *N*-sodium hydroxide for neutralisation, hence the values of the molecular proportion were calculated from the titration results obtained in the different experiments, and as these results expressed in terms of percentage of isomeric change are given under table I, the full details would be of no particular interest and have therefore been omitted.

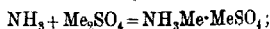
When ammonium methyl sulphate was heated to about 100° and upwards, a slight evolution of gas commenced after a few minutes' heating, and continued very slowly to the end of the experiment; this was found to be ethylene, the result of secondary decomposition, namely,



which to a very slight extent accompanies the main isomeric change. From 20 grams of ammonium methyl sulphate, after heating under the most favourable conditions, 8.9 grams of methylaniline hydrochloride were ultimately obtained, corresponding with 87.5 per cent. of the theoretical yield for complete isomerisation; hence the secondary decomposition referred to above has no serious effect on the main change.

#### *Preparation of, and Action of Heat on, Methylanilmonium Methyl Sulphate.*

This salt was readily prepared, in quantitative yield, by passing a current of dry ammonia into a solution of pure methyl sulphate in about fifteen times its volume of benzene until the product, on keeping for one hour, had a slight odour of ammonia, the flask containing the solution being immersed in ice-cold water. The salt gradually separated in micro-crystalline form; it was quite colourless, neutral in reaction, and gave an absolutely negative test when tested with barium chloride solution. The dry salt melted at 52°, and is very hygroscopic; its purity was confirmed by analysis and hence the reaction is correctly represented by the equation:



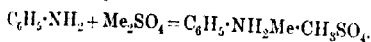
the formation of some ammonium methyl sulphate, recorded

son and Lundvaal (*loc. cit.*), was probably due to the presence of methyl hydrogen sulphate in the ester used by them. The examination of the progress of the isomeric change when tetramethylammonium methyl sulphate is heated was carried out exactly in the case of the ammonium salt; the results so obtained are given under table II.

#### *Interaction of Amines and Methyl Sulphate.*

The ester used in these experiments was purified from any acid impurities by shaking it with a solution of sodium hydroxide until neutral; the separated ester was then dried over anhydrous sodium sulphate, and used directly without redistillation.

*Expt. I. Aniline and Methyl Sulphate* (equal molecular proportions). To a solution of 9.3 grams of freshly distilled aniline in 100 c.c. of pure benzene, 12.6 grams of methyl sulphate dissolved in 100 c.c. of benzene were added; there was very slight development of heat, and after a short time, minute, thin, glistening plates began to separate. After twenty-four hours these were collected, washed with benzene, and dried over sulphuric acid and afterwards for a short time in a vacuum. The weight obtained was 21.1 grams, which theory requires 21.9 grams if the reaction proceeded in accordance with the equation:



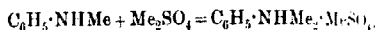
An aqueous solution of the product gave no precipitate with barium chloride solution, and on the addition of bleaching-powder solution and a few drops of dilute sulphuric acid, a deep indigo-blue colour was developed,\* a reaction characteristic of methylaniline ( $\text{C}_6\text{H}_5\text{NSO}_4 = 44.02$ .  $\text{C}_6\text{H}_5\text{NSO}_4$  requires  $\text{SO}_4 = 43.83$  per cent.). Tetramethylammonium methyl sulphate melts at  $159^\circ$ , and undergoes isomeric change very readily; this was strikingly demonstrated in the benzene filtrate from the preparation, which retained a quantity of the salt in solution, in the following manner: a portion of the benzene solution was evaporated to dryness on the water-bath, and the residue gave a copious precipitate with barium chloride solution, and, on addition of bleaching-powder solution, a deep orange colour was at once developed, a reaction characteristic of methylaniline. The original benzene solution when shaken with distilled water gave no reaction with barium chloride, but when previously heated for a few minutes on the water-bath and shaken with water, on applying the test reagent a precipitate

\* Generally stated that methylaniline gives no colour with bleaching-powder solution, but this is only true of the free base; on acidification an intense blue colour is quickly developed.

of barium sulphate was immediately formed as a result of isomeric change.

The experiment was repeated, using an excess of aniline; the weight of crystalline precipitate obtained was practically the same as before, the excess of aniline being found unchanged in the benzene filtrate, thus proving that the interaction takes place strictly in accordance with the equation given above, and that failure to recognise the isomerisation which takes place was responsible for the erroneous explanation of the change given by Ullmann (*loc. cit.*).

*Expt. II. Methylaniline and Methyl Sulphate* (equal molecular proportions).—To 10.7 grams of pure methylaniline dissolved in 75 c.c. of benzene, 12.6 grams of methyl sulphate dissolved in its volume of benzene were added; a clear, pale yellow oil immediately separated, without any appreciable evolution of heat; after twenty-four hours this was collected. The weight of oil was 32 grams; the theoretical yield of phenyldimethylaniline methyl sulphate formed in accordance with the equation



would be 23.3 grams. The oil when added to water rapidly dissolved with the separation of some benzene, and any attempt to expel the latter from the oil by heat was accompanied by evolution of isomeric change having taken place during the process, leaving the oil for a week in a vacuum over sulphuric acid; the product quite free from benzene was finally obtained. The residue, which showed no signs of crystallisation, was not solid but gave all the reactions of a salt of dimethylaniline, and the product could be detected in the original benzene separated from the oil, the yield of which corresponded very closely with the amount of the salt with a molecular proportion of benzene; it would require 31.1 grams. This property of forming a stable compound with benzene has already been noticed by Claessens and Lundvaal (*loc. cit.*) in the case of ethylaniline ethyl sulphate.

*Expt. III. Dipropylamine and Methyl Sulphate* (equal molecular proportions).—This experiment was carried out as in the previous case, with 10.1 grams of dipropylamine and 12.6 grams of methyl sulphate; a clear, almost colourless oil quickly separating with evolution of heat. The yield of oil was 30.8 grams, whilst the theoretical yield of methyldipropylammonium methyl sulphate would be 22.7 grams, and for a compound with one molecular proportion of benzene 30.5 grams. In this case also an attempt to expel benzene from the oil by heat was accompanied by isomeric change. The product, freed from benzene by the means mentioned in Expt. II, was a viscous liquid, the aqueous solution of which

precipitate with barium chloride solution, and on distillation potassium hydroxide gave methyldipropylamine, which was confirmed by the analysis of its hydrochloride (Found, Cl = 23.44. Calcd., Cl = 23.43 per cent.).

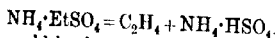
Experiments II and III were repeated, using an excess of the reactive amine; in each case this excess was found unchanged in the benzene separated from the precipitated oil, proving that secondary amines also the reaction with methyl sulphate is in equal molecular proportions and in accordance with the general equations already given.

*Note on Ammonium Ethyl Sulphate and Ammonium n-Propyl Sulphate.*

Pure ammonium ethyl sulphate was readily prepared in very good yield by directly neutralising crude ethyl sulphuric acid (prepared in the usual manner) with commercial ammonium carbonate, absolute alcohol being used for the extraction and recrystallisation of the ammonium salt. The yield was 58 grams of the compound from 50 grams of ethyl alcohol, no attempt being made to recover a further quantity from the mother liquor. The salt crystallises from alcohol in thin, flat, rhomboidal prisms, which have been easily obtained in a length of 4–5 cm., and showing a brilliant, satin-like lustre.

Ammonium ethyl sulphate melts at 97° (not 62°, as stated in previous works of reference), and is not notably hygroscopic, which is contrary to the published statements.

When heated the salt decomposed rapidly at about 220° with evolution of ethylene; after fifteen minutes at this temperature amount of decomposition was 55 per cent., in accordance with the equation:



Diethylamine could be detected in the residue, thus proving the absence of any isomeric change.

Ammonium n-propyl sulphate (m. p. 132°) was obtained in good yield from crude n-propylsulphuric acid in a manner similar to that stated above. The pure salt, which is very hygroscopic, decomposed rapidly at 150–160° with the evolution of propylene and without any evidence of isomeric change.

STRENGTH CHEMICAL LABORATORY,  
TRINITY COLLEGE, DUBLIN.

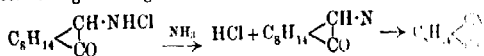


CCLIX.—*Studies in the Camphane Series.* P<sub>2</sub>  
 XXXVI. *N*-Chloroaminocamphor.

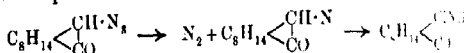
By MARTIN ONSLOW FORSTER and MAX SCHLAEPFER.

THE subject of this communication was produced as the result of attempts to shorten the process for obtaining camphor (camphorylazoimide), the original method (T. 1881, 826) being too circuitous for ordinary application.

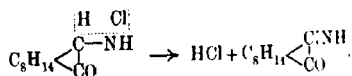
The possibility of replacing the halogen in  $\alpha$ -chloro- $\alpha$ -bromocamphor by heating these materials with sodium was first tested, without success, when Raschig's description of a method for preparing hydrazine (D.R.-P. 198307; A. 19, 1029) suggested the production of camphorylhydrazine, from which by the action of nitrous acid, camphorylazoimide should result, the principle rendered familiar by Curtius. On adding  $\alpha$ -chloroamine to dissolved aminocamphor, however, a substance was precipitated, and instead of having the properties expected of camphorylhydrazine, was found to consist of  $\alpha$ -aminocamphor. There remained a possibility of arriving at camphorylhydrazine by the action of ammonia on the chloro- $\alpha$ -aminocamphor, but experiment showed that the removal of hydrogen chloride takes place in such a way as to produce iminocamphor, the preparation of which substance a very convenient method has been brought to light:



The reaction, in fact, is directly comparable with that by which iminocamphor was obtained originally:



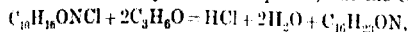
the wrenching away of two atoms—nitrogen alone in the case of triazocamphor, hydrogen and chlorine in the case of  $\alpha$ -aminocamphor—so disturbing the affinity relations of the nitrogen as to cause migration of hydrogen from the neighbouring carbon. The alternative explanation:



was tested by the preparation of camphorylacetyl nitrogen (aceto- $\alpha$ -chloroaminocamphor) and treatment of this compound with ammonia, which led simply to the regeneration of  $\alpha$ -aminocamphor.

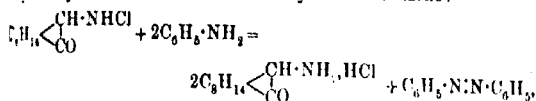
camphor instead of aceto-iminocamphor, or camphorquinone acetamide.

Although not the first representative of its class, the simplest member, methylchloroamine, having been prepared in 1893, we have that chloroaminocamphor is probably the first material of this type to be obtained in crystalline form, and, as might be expected, it is a very active and unstable substance, oxidising hydrogen iodide and sulphurous acid in the manner of an acylated or alkyl nitrogen chloride. It rapidly undergoes a spontaneous change, the undissolved material being transformed in the course of a few hours into a honey-like mass, whilst solutions in carbonous quickly deposit aminocamphor hydrochloride, and retain the anhydride of cyanolauronic acid together with crystallisable products. In acetone the chloroamine also changes to aminocamphor hydrochloride, accompanied by a crystalline compound (m. p. 155°) having the composition  $C_{16}H_{23}ON$ ; this has not been identified with any known compound, but the equation:



will account for a product having this empirical formula.

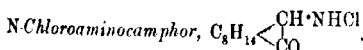
Whilst ammonia converts chloroaminocamphor into iminocamphor, aromatic amines are oxidised by the substance, which takes hydrogen from the amino-group and passes into aminocamphor hydrochloride. Thus aniline yields azobenzene:



but phenylhydrazine loses its nitrogen.

During a few days' suspension in water, the chloroamine changes to a crystalline material melting at 95°, along with aminocamphor hydrochloride. The new compound, which is produced when chloroaminocamphor is dissolved in sulphuric acid, is a derivative of nitrogen chloride, and is related to camphor imide, yielding that substance when heated at 100°. Owing to its unstable character, and the consequent difficulty attending analysis, we cannot be certain of the empirical formula, although  $H_{16}O_4NClH_2O$  is indicated.

#### EXPERIMENTAL.



An acid solution of aminocamphor hydrochloride prepared from grams of isonitrosocamphor, as already described (T., 1905, 87,

113), was chilled with ice and treated with chloroamine (330 c.c. of a sodium hypochlorite solution (containing 32 grams available chlorine per litre) and 6 c.c. of ammonia (0.88 g. to 50 c.c. The solution remained alkaline to litmus, and a colourless oil separated immediately and rapidly solidified. After three hours in ice, during which period separation of the chloroamine was complete, the substance was collected, roughly on earthenware, and for all ordinary purposes was used in this form, 20 grams being the amount usually obtained.

As the substance is extremely unstable, purification operations must be completed in one day. Such specimens were prepared by mixing the ingredients overnight, leaving the suspended solids in the ice-chest, and filtering early the following morning. A roughly dried material was immersed in cold petroleum (40–50°) in quantity insufficient for dissolution, and then stirred with calcium chloride, the amount of which may be varied to develop with the associated water enough heat to dissolve the excess of the chloroamine without perceptibly raising the temperature of the solution. This was filtered and rapidly evaporated under diminished pressure, when there separated radial aggregates of colourless needles melting at 43° and decomposing violently at 85°:

0.2720 gave 0.6012  $\text{CO}_2$  and 0.1976  $\text{H}_2\text{O}$ .  $\text{C} = 60.3$ ;  $\text{H} = 8.1$

0.3042 „ 18.8 c.c.  $\text{N}_2$  at 23° and 758 mm.  $\text{N} = 7.0$

0.2641 contained 0.0442 available chlorine.  $\text{Cl} = 16.7$

$\text{C}_{10}\text{H}_{16}\text{ONCl}$  requires  $\text{C} = 59.6$ ;  $\text{H} = 7.9$ ;  $\text{N} = 6.9$ ;  $\text{Cl} = 17.6$  per cent.

Chloroaminocamphor is sparingly soluble in cold water, but it solves very freely in all organic media; it liberates iodine from aqueous potassium iodide immediately, but before titrating this liquid with sodium thiosulphate it is better to add alcohol and a few drops of glacial acetic acid. Even the purified compound cannot be preserved, because it changes in the course of a few hours to a yellow resin, liberating chlorine and hydrogen chloride; this alteration takes place alike, whether it is exposed to the air or situated in a desiccator containing soda-lime, and occurs if the material is widely and loosely distributed.

Although the conditions of preparation appear to preclude the possibility of the foregoing substance being the hypochlorite aminocamphor, the hydrochloride of the base was mixed in aqueous solution with sodium hypochlorite alone; this precipitated an oil which did not become solid, and which underwent explosive decomposition even while suspended in water.

*Action of Sodium Sulphite.*—The simple relation between the chloroamine and the original base is established by the reaction

of the latter under the influence of sodium sulphite. When the prepared chloroaminocamphor is immersed in a solution of salt, the hard granules rapidly become pasty and afterwards the odour of sulphur dioxide being noticeable. With further time the oil disappears, leaving a small proportion of camphorquinone, whilst the main bulk of the chloroamine is removed in the filtrate by salts of aminocamphor.

*Decomposition in Benzene.*—Solutions of the chloroamine in some media change at various rates, and always yield aminocamphor hydrochloride. Thirty-four grams of freshly prepared, freshly dried chloroaminocamphor were dissolved in 100 c.c. of benzene, dried with calcium chloride, filtered and left in a desiccator containing soda-lime. In the course of a few hours aminocamphor hydrochloride began to separate in colourless needles, increasing with passage of time until about 14 grams had accumulated after the lapse of nearly nine weeks; meanwhile the air in the desiccator liberated iodine from potassium iodide, and the solution remained active during more than four weeks. On evaporating the filtered benzene there was deposited a bright yellow, waxlike mass, and although this weighed more than 12 grams, about 1 gram of crystalline material was obtained from it. A small proportion of this was camphorquinone, separated by adding the honey successively with small quantities of light petroleum, which dissolved that substance; the residue became hard and granular, and on being dissolved in a very small quantity of methyl alcohol was deposited slowly in colourless crystals, and on recrystallisation from the same solvent, formed colourless plates melting at  $174^{\circ}$  (Found, C=69.3; H=8.3; N=8.3.  $\text{C}_{15}\text{H}_{13}\text{NO}_2$  requires C=69.8; H=8.1; N=8.1 per cent.). The compound was thus identified as the anhydride of cyanolauronic

acid. The change which chloroaminocamphor undergoes in petroleum follows the same course, yielding aminocamphor hydrochloride and a small proportion of the anhydride of cyanolauronic acid.

*Decomposition in Acetone.*—Fifty grams of the chloroamine were dissolved in 50 c.c. of acetone at zero, the liquid slowly becoming brown. After twelve hours in the ice-chest a heavy, almost solid oil had separated, and as this did not dissolve on adding more acetone the liquid was set aside during one week, when it became homogeneous and much darker, whilst 7.3 grams of pale brown crystals separated. The filtrate affected the eyes in the manner of chloroacetone, and did not deposit more solid after weeks at zero; it was therefore diluted largely with water, when precipitated a brown tar, and from this, by rubbing with

cold methyl alcohol, a further 2 grams of crystalline material was recovered. On treating the accumulated solid with aqueous ammonia (1:1), 3.5 grams remained, and the filtrate contained camphor hydrochloride. The solid residue dissolved freely in boiling alcohol, and crystallized in lustrous, very pale brown needles melting at 155°:

0.2070 gave 0.5931  $\text{CO}_2$  and 0.1723  $\text{H}_2\text{O}$ .  $\text{C}=78.1$ ;  $\text{H}=9.1$

0.1917 „ 9.9 c.c.  $\text{N}_2$  at 23° and 763 mm.  $\text{N}=5.8$

$\text{C}_{16}\text{H}_{23}\text{ON}$  requires  $\text{C}=78.4$ ;  $\text{H}=9.4$ ;  $\text{N}=5.7$  per cent.

The substance is freely soluble in benzene or ethyl acetate and dissolves readily in boiling petroleum, from which it is easily crystallized.

*Action of Ammonia.*—Freshly prepared chloroaminocamphor was covered with ammonia (0.88) and stirred at intervals, becoming oily in less than one hour, afterwards changing to a hard white aminocamphor; as this substance is extremely unstable, and cannot be recrystallized, it was identified (1) by quantitative conversion into camphorquinone and ammonia, and (2) by the characteristic magenta coloration developed with formaldehyde and sodium methoxide (T., 1908, 93, 250).

*Action of Amines.*—As already stated, the foregoing experiment was made with the object of preparing camphorylhydrazine, and the result was totally unexpected. The action of various amines was therefore studied, but the most definite result was obtained with aniline. Nine grams of chloroaminocamphor were dissolved in ether, and having been dried with calcium chloride, the solution was mixed with 8 grams of aniline. On the following day 2 grams of aminocamphor hydrochloride were removed by filtration, the dark brown liquid, when freed from ether, was treated with dilute hydrochloric acid to remove excess of aniline. The residue became harder when rubbed with a small quantity of alcohol and having been drained from the latter, was extracted with petroleum, which deposited azobenzene on evaporation.

When treated under similar conditions with diphenylamine mixture of aminocamphor hydrochloride with ammonium chloride separated, and these salts were precipitated also by azobenzene amine, but azonaphthalene could not be identified in the brown, viscous material deposited by the filtrate. With phenylhydrazine the action was extremely violent at the ordinary temperature, but on mixing dilute ethereal solutions of the materials at zero very slowly, aminocamphor hydrochloride was precipitated and a steady liberation of gas took place.

*Action of Water.*—Ten grams of chloroaminocamphor was covered with about 30 c.c. of water and stirred at intervals. A

few days the substance, at first granular and dense, had swollen in the liquid and had become soft; the following morning it had become dense again and very hard, whilst flat, colourless needles were suspended in the pale yellow liquid. The solid weighed 1.5 grams whilst the filtrate, after extraction twice with ether to remove a very small quantity of camphorquinone, deposited on evaporation 4 grams of aminocamphor hydrochloride mixed with a very small proportion of ammonium chloride. Meanwhile the colourless crystals, a less impure form of the hard, granular mass, were found to set free iodine from potassium iodide, and when dissolved in ethyl acetate, using the device already adopted in the case of chloroaminocamphor, petroleum precipitated flat, colourless prisms in stellate aggregates. Newly crystallised, the substance melted at  $95^{\circ}$ , evolving gas, but when preserved in a desiccator containing soda-lime, it changed into a material which melted at  $72^{\circ}$ , did not liberate iodine from potassium iodide, and when dissolved in hot water gave the imide of camphoric acid (m. p.  $55^{\circ}$ ); the latter is produced also when the substance is heated with  $\text{PCl}_5$ , chlorine being liberated:

0.3848 gave 0.3887  $\text{CO}_2$  and 0.1471  $\text{H}_2\text{O}$ .  $\text{C}=52.8$ ;  $\text{H}=8.1$ .

0.1522 " 0.3 c.c.  $\text{N}_2$  at  $18^{\circ}$  and 771.5 mm.  $\text{N}=6.0$ .

0.3460 contained 0.04985 available chlorine.  $\text{Cl}=14.4$ .

$\text{C}_{16}\text{H}_{16}\text{O}_2\text{NCl}\cdot\text{H}_2\text{O}$  requires  $\text{C}=51.1$ ;  $\text{H}=7.7$ ;  $\text{N}=6.0$ ;  
 $\text{Cl}=15.0$  per cent.

We ascribe the indeterminate result of this analysis to the difficulty of removing the last traces of petroleum in a substance, owing to its excessive instability, must be analysed immediately. The compound is freely soluble in organic media, but differs from chloroaminocamphor by its sparing solubility in cold petroleum. It is also produced when chloroaminocamphor is dissolved in concentrated sulphuric acid; 10 grams of the freshly prepared material were added in small quantities to 50 c.c. of ice-cold acid, which was shaken vigorously during the process, chlorine being liberated. After half-an-hour, when effervescence ceased, the liquid was poured on crushed ice, which precipitated a colourless oil, partly solidifying; the product weighed 3.3 grams, and when crystallised from acetone diluted with water formed lustrous needles melting at  $95^{\circ}$ .

*N*-Chloroaceto-aminocamphor,  $\text{C}_8\text{H}_{14}\text{CH}(\text{CO}\cdot\text{CH}_3)\text{NCl}$ .

The finely powdered acetyl derivative of aminocamphor was suspended in aqueous sodium bicarbonate at zero, and treated with an ice-cold solution of sodium hypochlorite; after twelve hours the product was filtered, washed, and dissolved in cold methyl

alcohol, from which water precipitated lustrous, silky needles melting at  $78^{\circ}$ :

0.1500 contained 0.0218 available chlorine.  $\text{Cl}=14.5$ .

$\text{C}_{12}\text{H}_{18}\text{O}_2\text{NCl}$  requires  $\text{Cl}=14.5$  per cent.

The substance is freely soluble in petroleum, acetone, or methyl alcohol, and liberates iodine from potassium iodide immediately. Ammonia does not transform it into aceto-iminoacetylphenylhydrazide, but merely regenerates the acetyl derivative of aminocamptophylline.

In conclusion, we desire to express our thanks to the Members of the Royal Institution for their courtesy in placing a laboratory at our disposal.

THE DAVY-FARADAY LABORATORY  
OF THE ROYAL INSTITUTION, W.

#### CCCLX.—*The Corrosion of Iron and its Application to Determine the Relative Strengths of Acids.*

By JOHN ALBERT NEWTON FRIEND and CHARLES WILLIAM MARSHALL.

It is now a matter of common knowledge that fairly concentrated solutions of sodium hydroxide or carbonate will inhibit the corrosion of iron. In 1911 attention was drawn to the fact that the corrosive action of aqueous solutions of metallic salts of any concentration may be completely inhibited by the addition of small quantities of alkaline hydroxide (Friend, *J. Iron and Steel Inst.*, 1911, 1). In view of the close connexion between corrosion and neutralization, it seemed of interest to determine the minimum quantities of alkali required to inhibit the corrosive actions of different salts and to discover whether or not any relationship exists between these quantities and the relative strengths of the acids and bases constituting the salts.

To this end numerous experiments were carried out by exposing small pieces of iron to the action of different salt solutions with varying quantities of sodium or potassium hydroxide; but the results were too uncertain and irregular to be of any value. This was ultimately traced to the presence of carbon dioxide in the solutions, which was readily absorbed in irregular quantities by the alkalis and hydroxides. With the carbonates and borates of the alkalis, however, very trustworthy results were obtained, capable of repetition an indefinite number of times. Ultimately, therefore, these were used as inhibitors, the carbonates proving the most convenient both on account of their simpler constitution and their greater solubility in water.

The procedure was as follows: Five c.c. of a  $N/10$  solution of a sodium salt were introduced by means of a pipette into each one of a series of five hard-glass tubes containing 1, 2, 3, 4, and 5 c.c. standard sodium carbonate solution respectively. The tubes had been previously steamed out in order to remove any traces of organic matter—a precaution that was found to be absolutely necessary. The volume of each solution was now made up to 10 c.c. by the addition of freshly distilled water. Finally, pieces of iron foil, measuring 1 cm. square, which had been well polished with old emery paper and not touched with the fingers, were added, one to each tube, and the latter was sealed with a rubber cork. It was found important to add the iron last of all after thorough mixing of the solutions employed, as contact with different solutions before mixing appeared to exert some influence on the surface of the metal rendering the results uncertain. For the same reason the pieces of iron were never used twice (see, T., 1912, 101, 50). The sealed tubes were kept in a box at uniform temperature, and subject in the daytime to diffused sunlight. After two or three days they were examined. The iron in the first one, two, three, or four tubes was usually found to be corroded, but that in the remaining tubes was not.

The tubes could now, as a general rule, be kept for months without any further pieces of iron undergoing oxidation. The corroded tubes in cases distant from the end-point gave signs of further corrosion; but those close to the end-point appeared to undergo no change. This is remarkable in view of the fact that only a small fraction of the oxygen in the air in the tubes had been absorbed during corrosion. Sulphides yielded a very clear end-point during the first few days, but after prolonged keeping the iron had previously shown no tendency to corrode were found to become oxidised, thus altering the end-point very considerably. The end-point was ultimately traced to slow oxidation of the sulphite to sulfate.

By repeating the experiments with intermediate quantities of carbonate it was found possible to determine to within about 5 per cent the amount of carbonate required to inhibit corrosion under particular conditions of the experiments. The presence of rust was always easy to detect after a little practice, and it is not probable that results of still higher accuracy could be obtained by the use of more finely graduated instruments.

The best method of observation was found to consist in exposing the tubes to powerful light, the tubes being continually rotated in order that the spots of rust should not be overlooked. These spots were



often minute, particularly near the end-points in the case of the stronger acids, frequently occurring at corners of the metal in contact with the glass. In the case of the weaker acids the amount of rust produced was, as a general rule, considerably greater, rendering the end-point more easy to detect.

The rust formed varied very much in appearance. With the phosphates it was white, with an under-layer of green in very dilute solution. Sulphites gave a green rust, which became red on standing. Chlorides, nitrates, and sulphates yielded reddish-brown rust; iodides, black.

The results obtained with sodium salts, using sodium carbonate as inhibitor, are given in tables I and II. The concentrations of the various salts are expressed in terms of a normal solution, and the amounts of sodium carbonate required to be present in 10 c.c. of such solutions in order just to inhibit corrosion are, for the sake of convenience, expressed both as c.c. of a molecular solution, and relatively to one another, the highest amount being taken as 100.

In actual practice, in the *N*/100 tests, 1 c.c. of a *N*/10 solution of the salt was taken, varying quantities of the carbonate solution added, and the volume made up to 10 c.c. Thus a better comparison was obtainable than by making a new solution of the salt.

TABLE I.  
*Sodium Carbonate as Inhibitor.*

Sodium salts, <i>N</i> /20.	Concentration of $\text{Na}_2\text{CO}_3$ .	Relative concentration of $\text{Na}_2\text{CO}_3$ ( $\text{NaCl} = 100$ ).	Relative strength of free acid ( $\text{HCl} = 100$ ).
Chloride .....	1.35	100	100
Iodide .....	1.20	88.9	98
Bromide .....	0.975	72.2	98
Nitrate .....	0.725	53.7	98
Sulphate .....	0.700	51.85	70
Fluoride .....	0.525	38.9	100
Acetate .....	0.120	8.9	4
Sulphite .....	0.025	1.9	2

TABLE II.  
*Sodium Carbonate as Inhibitor.*

Sodium salts, <i>N</i> /100.	Concentration of $\text{Na}_2\text{CO}_3$ .	Relative concentration of $\text{Na}_2\text{CO}_3$ .	Relative strength of free acid ( <i>N</i> /100 $\text{HCl} = 100$ ).
Chloride .....	0.525	100	100
Iodide .....	0.500	95.2	98
Bromide .....	0.475	90.5	97.5
Sulphate .....	0.400	76.2	82.5
Nitrate .....	0.375	71.4	98
Fluoride .....	0.375	71.4	17
Acetate .....	0.070	13.3	4
Sulphite .....	0.035	6.7	2

Consideration of the above tables reveals the interesting fact that in the salts are arranged in descending order of inhibiting capacity concentrations, not only are they in the order of the increasing electrical conductivity of their acids, but the relative values of carbonate solution bear a general relationship to the actual values found for the strengths of the acids by electrical conductivity and hydrolysis methods.

It will also be observed that on increasing the dilution from  $N/100$  the relative amounts of the carbonate required by different salts steadily approach that required by the sodium carbonate, which is taken as the standard. In other words, the true strengths of the acids tend to approach equality with each other as the ionic theory requires. It is interesting to note that the more dilute solutions the nitrate and sulphate exchange reactions. The low position of the nitrate in the  $N/20$  solution is remarkable, and one is led to ask whether or not passivification has caused the results, nitrates being well known passivifiers of iron. Still more exceptional are the values found for the sulphite in  $N/20$  and  $N/100$ -solution. The figures given in the final columns of tables I and II, however, are based on freezing-point measurements, and are therefore less strictly comparable.

The results obtained with sodium borate as inhibitor were, on the whole, very similar. The concentration of the sodium salts  $N/100$ , the inhibiting quantities of borax being expressed as if a molecular solution present in 10 c.c. of the mixed solutions (table III).

TABLE III.  
*Borax as Inhibitor.*

Sodium salts, $N/100$ .	Concentration of borax.	Relative concentration of borax.	Relative strengths of free acids in $N/100$ -solution.
NaCl.....	0.36	100	100
Na <sub>2</sub> SO <sub>4</sub> .....	0.315	87.5	97.5
NaNO <sub>3</sub> .....	0.31	86.1	82.5
Na <sub>2</sub> CO <sub>3</sub> .....	0.33	91.7	98
Na <sub>2</sub> SO <sub>3</sub> .....	0.195	54.2	98
Na <sub>2</sub> CO <sub>3</sub> .....	0.100	27.8	17
Na <sub>2</sub> SO <sub>3</sub> .....	0.070	19.4	4
Na <sub>2</sub> CO <sub>3</sub> .....	0.050	13.9	83
Na <sub>2</sub> CO <sub>3</sub> .....	0.045	12.5	0.8*
			30†

The relatively low solubility of borax in water renders it less efficient as an inhibitor than sodium carbonate, by restricting

its dissociation constant  $k = 1.8 \times 10^{-5}$  (Walker and Cornack, T., 1900,

giving  $k = 5 \times 10^{-4}$  (Thiel and Strohecker).

the range of concentrations. When the above results are compared with those in table II of like concentration it will be seen that a reasonably close similarity obtains. With the exception of the iodide and bromide, which now interchange positions although the difference between them is very slight, all the other acids take the same positions. It is interesting to note that by this method a value for carbonic acid is obtainable, which, however, is very low.

Thiel and Strohecker (*Ber.*, 1914, 47, 945) have recently adduced evidence in favour of the supposition that the true dissociation constant of carbonic acid is much greater than that usually ascribed to it, since only a small percentage of dissolved carbon dioxide exists as carbonic acid in aqueous solutions of the gas.

Assuming this to be correct, the high value for sodium carbonate in table III is readily understood, because practically the whole of the carbon dioxide is "fixed," and therefore ionised in the solution.

Experiments with potassium salts, using potassium carbonate as inhibitor, yielded closely similar results to those detailed in table I in so far as the relative quantities of inhibitor were concerned, but the absolute quantities were greater.

The concentrations of the potassium salts were  $N/20$ , and in table IV the amount of potassium carbonate required to prevent inhibition is expressed as c.c. of a molecular solution in 10 c.c. of the mixed solution.

TABLE IV.  
*Potassium Carbonate as Inhibitor.*

Potassium salts, $N/20$ .	Concentration of $K_2CO_3$ .	Relative concentration of $K_2CO_3$ .	Relative strength of free acids $N/20$ solution.
Chloride.....	1.85	100	100
Bromide.....	1.70	92	95
Iodide.....	1.70	92	95
Nitrate.....	0.85	46	50
Sulphate.....	0.775	42	50
Fluoride.....	0.675	31	40
Acetate.....	0.225	12	2
Sulphite.....	0.050	2.7	5

Many salt solutions, such as sodium acetate, borate, carbonate and sulphide, whilst capable of inhibiting corrosion when fairly concentrated, cannot do so if fairly dilute. It was of interest to determine accurately the concentrations at which this action just begins in the case of the above-mentioned salts, in order to discover whether or not the same ionic relationship holds in the experiments with an added inhibitor. This was accomplished by immersing small pieces of iron foil in 10 c.c. of varying concentrations of the different salts, and noting the lowest concentration

which corrosion was permanently inhibited. The results obtained are given in table V.

TABLE V.

*Auto-inhibition.*

	Inhibiting concentration of salt.	Relative concentration of salt taking acetic acid as 8.9 (Table I).	Percentage ionisation of free acids at dilutions given in Col. I at 18°.	Relative strengths of free acids at dilutions given in Col. I (HCl 100.)
	(i.)	(ii.)	(iii.)	(iv.)
General salt	0.30 N	8.9	0.77	0.87
arsenite	0.06 "	1.8	55	58
phosphite	0.06 "	1.8	42	44
borate	0.05 "	1.5	50	53
arsenate	0.021 "	0.62	0.55	0.57
phosphate	0.009 "	0.27	0.07	0.07

is not strictly logical to compare column i with column iv, since in the former acetic acid is taken as the standard although its concentration is at least five times as great as that of any other acid, whereas in column iv due allowance is made for the varying degrees of dilution. In the circumstances, however, it is the only method possible, and since weak acids are being dealt with the error will not be unduly great.

It will be observed that the sulphite gives the same result as by the carbonate method (table I), and the concentration is practically the same. The result for sodium carbonate is much lower than in table II), and approaches more nearly the usually accepted value for carbonic acid. The difference in the concentrations in the case of the arsenate (tables III and V) is far too small to account for the variation. The values for the arsenate and phosphate are in agreement with that for the sulphite, the three free acids being of equal strength according to conductivity measurements. The figures given in table V, however, indicate that the acids are weaker even than acetic acid, which is not really the case. On the other hand, the value obtained for the borate is four times as high as that for the free acid. It would appear, therefore, that these results are not comparable with those obtained by the use of inhibitors.

Other experiments have also been carried out with the object of determining the quantities of sodium carbonate required to prevent corrosion in the presence of varying quantities of the sodium salt. The results are given in table VI, the concentrations of the acids being expressed in terms of normality, whilst the inhibiting quantities of sodium carbonate in 10 c.c. of the salt solutions are, for the sake of convenience, expressed as c.c. of a normal solution.

TABLE VI.

Sodium salt.	N.	N/2.	N/2.5.	N/3.3.	N/4.	N/5.	N/10.	N/17.	A.S.
Chloride.....	—	—	16.0	—	—	8.0	—	—	2.7
Nitrate .....	10.0	7.6	5.6	—	—	3.6	—	—	1.0
Sulphate .....	4.8	3.2	2.8	—	—	2.4	—	—	1.4
Fluoride .....	—	1.4	—	—	1.4	—	1.4	—	1.0
Sulphite .....	—	—	—	—	—	—	—	0.0*	0.0
Acetate .....	—	—	—	0.0*	—	—	—	—	0.0

\* Auto-inhibition.

If these results are plotted diagrammatically a distinct balance can be traced to the specific conductivity curves of the acids when drawn from the data published by Kohlrausch. Unfortunately, owing to the limited solubility of the salts employed, it is not possible to employ high concentrations, and thus to push the analogy further. It is interesting to observe, however, that the acetate curve indicates the existence of a maximum effect, as to that observed by Kohlrausch, but at a different concentration.

No attempt is here made to explain these results. The authors wish, at this stage of their work, merely to draw attention to an interesting connexion between corrosion and ionisation.

In conclusion, the authors have pleasure in expressing their indebtedness to the Research Fund Committee for a grant which defrayed the greater part of the expense entailed by this work.

VICTORIA INSTITUTE,  
WORCESTER.

CCLXI.—*Rotatory Power and Refractivity. Part I.—The Rotatory Powers, Refractivities and Molecular Solution-volumes of Cinchonidine and Berberine in Certain Solvents.*

By DAVID HENRY PEACOCK.

THE close connexion between the physical expressions defining the electromagnetic theory of light for the optical properties of a substance has long been noticed. In practice it is found that a molecular structure as is connoted by the term "conjugated double bonds" produces an exaltation of the magnetic and rotatory powers and of the refractivity. An investigation of the rotatory powers, refractivities, and molecular solution-volumes was commenced by the author in order to discover if there was

\* In Kohlrausch's experiments the maximum specific conductivity was at a concentration of 2.5N.

connection between the two optical properties. While this work was in progress a series of papers appeared by Livens (*Phil. Mag.*, [3, (vi), 25, 817 *et seq.*]), in which on theoretical grounds an expression was deduced connecting refractivity and rotatory power. If  $n$  is the refractive index of a solution of density  $d$  containing a solute in concentration  $c$ , then:

$$\frac{n^2 - 1}{a(n^2 - 1) + 1} = rc + s(d - c) \quad (1)$$

and  $[a]$ —specific rotation per unit length for light of frequency  $\nu$  is then:

$$[a] = r'p^2 \frac{rc + s(d - c)}{[1 - a(rc + s(d - c))]^2} \quad (2)$$

where  $r$  and  $r'$  and  $a$  are constants depending on the solute, and  $s$  is a constant depending on the solvent. Then we have:

$$[a] = \frac{r'p^2a}{2} (n^2 - 1)(n^2 - 1 + 1/a) \quad (3)$$

These equations are all given in Livens' paper. From this last equation it will be seen that specific rotatory power should vary in the same manner as the expression  $(n^2 - 1)(n^2 - 1 + 1/a)$ . No data have been hitherto available to test this, and in the present paper a few simple cases are considered; the work is still in progress, and more data are being collected.

From the first equation it will be seen that it should be possible to calculate the constant  $a$  from the refractivity alone. It is, however, more easily calculated from equation (3). If we put  $c = 0$  in equation (1) then we get:

$$\frac{n_0^2 - 1}{a(n_0^2 - 1) + 1} = sd_0 \quad (4)$$

an equation connecting  $a$  with the constants of the pure solvent.

On the other hand, putting  $c = 100$  per cent. in (1) we get an expression for the refractive index of the solute at 100 per cent. concentration. The quantities can also be deduced from the rotatory power, since we have from (3):

$$\begin{aligned} [a_1] &= (n_1^2 - 1)(n_1^2 - 1 + 1/a) \\ [a_2] &= (n_2^2 - 1)(n_2^2 - 1 + 1/a) \end{aligned} \quad (5)$$

Therefore if we know the value of  $[a_1]$  at a particular concentration  $c$  and of  $n_c$ , the refractive index at the same concentration,  $[a_2]$  or  $n_x$  at a concentration  $x$  can be found if either is known. In very dilute solutions it is difficult accurately to measure  $[a]$ , but from the above equation it can be deduced as the refractive index is susceptible of careful measurement; thus trustworthy values of  $[a]$  at infinite dilution can be obtained. Similarly, from the value of  $[a]$  in concentrated solutions the value at zero dilution

can be found by extrapolation, and from this the value of  $r$  at the same conditions deduced. This quantity may attain in usefulness, as hitherto the refractive indices of dissolved substances have been almost entirely deduced from the additive formula

$$\frac{M n^2 - 1}{d n^2 + 2} = \frac{M + l}{d_s} \frac{n_s^2 - 1}{n_s^2 + 2} - \frac{l}{d_0} \frac{n_0^2 - 1}{n_0^2 + 2}$$

where  $M + l$  is the weight of solution containing the gram-molecular weight  $M$  of the solute,  $l$  is the weight of the solvent of density and refractive index  $n_0$ , and  $d_s$  and  $n_s$  are those quantities for the solvent.

From equation (5) it will also be seen that the specific rotatory power can only be independent of the concentration in cases in which the refractive index of the solution is independent of the concentration; in other cases there should be variation with concentration although the amount of this variation cannot at present be predicted.

Pope and Gibson (T., 1912, 101, 1702) describe certain derivatives of *d*-sec.-butylamine which show practically no optical dispersion. It would be interesting to examine also the refractive constants of these derivatives in the light of equation (3) given above.

According to the theory on which the equations given above are deduced, the effect of concentration on specific rotatory power is explained solely by the variation in the velocity of transmission of light waves in the solution. When a beam of plane polarized light is split up on entering an active solution into two beams, oppositely circularly polarized light travelling at different velocities, the retardation, to which the rotation of the plane of polarization is due, is shown by this theory to depend on the optical properties of the solvent, and not merely on the active solute. Previous theories have explained the effects of concentration and of change of solvent by (1) electrolytic dissociation, (2) formation of molecular aggregates, and (3) changes in molecular symmetry due to the effect of the internal pressure of the molecule. In the present paper the data are not very numerous in the cases where a change of specific rotatory power with concentration occurs, but it has been pointed out that all the above theories ascribe the change to an actual variation of the forces acting within the active molecule, that is to say, to a change in  $r'$  (equation 3). If, therefore, the effect of concentration is due to the above causes, then equation (5) will no longer hold as  $r'$  will depend on  $c$ , and therefore  $[\alpha]$  will not be proportional to the quantity  $(n^2 - 1)/(n^2 + 1)$ . The results given in the present communication show that for the solutions examined  $[\alpha]$  is, within reasonable limits, proportional to

fraction expression, and therefore in those cases where  $[\alpha]$  depends on concentration the dependence is probably not due to the molecular changes usually invoked to explain this dependence, but is simply "to the variation in the velocity of transmission of light."

The rotatory powers of the solutions examined were measured in 10-cm. tubes at 25°, sodium light being used. The solutions were kept up in 25 c.c. flasks at 25°. The refractive indices of the solutions were measured in a Zeiss total reflection refractometer, as used for examining oils technically. The densities were measured in pycnometers holding about 10 c.c.

*Borneol, C<sub>10</sub>H<sub>18</sub>O.*

This was recrystallised from light petroleum. As also found by Kone (T., 1909, 95, 600), it was partly racemised. This does not alter the deductions in the present paper, as only ratios of rotatory powers are dealt with.

TABLE I.

*Alcohol Solutions.*

	$n_D^{25}$	$d_4^{25}$	$V_m$ c.c.	$[\alpha]_D^{25}$	$(n_D^2 - 1)(n_D^2 + 1)/\alpha$
16.2	0.275	1.3613	0.7889	150	(27.4°)
16	1.12	1.3635	0.7921	157	25.8
16	1.46	1.3636	0.7934	157	25.6
16	2.15	1.3669	0.7944	(165)	25.5
11	3.11	1.3682	0.7998	157	25.7
7	4.15	1.3711	0.8040	161	25.9
9	10.65	1.3872	0.8278	(144)	26.4
9	15.70	1.3993	0.8406	157	26.4

$p$  = concentration in grains per 100 grams.

TABLE II.

*Acetone Solutions.*

	$n_D^{25}$	$d_4^{25}$	$V_m$ c.c.	$[\alpha]_D^{25}$	$(n_D^2 - 1)(n_D^2 + 1)/\alpha$
17	0.43	1.3583	0.7860	158	27.6°
15	1.26	1.3613	0.7925	160	26.3
10	2.31	1.3623	0.7960	158	28.6
9	4.62	1.3675	0.8035	158	28.7
	6.73	1.3739	0.8113	159	27.0
	8.73	1.3791	0.8184	(175)	27.1
	17.47	1.4005	0.8493	159	27.2



TABLE III.

*Ethyl Acetate Solutions.*

$p$	$n_D^{20}$	$n_D^{25}$	$d_4^{25}$	$V_{90}$ c.c.	$[\alpha]_D^{25}$ ( $c_0 = 1$ )	$[\alpha]_D^{25}$ ( $c_0 = 1$ )
0.8699	0.44	1.3711	0.8953	161	28.27	0.000
2.2461	1.12	1.3719	0.8956	162	28.4	0.000
4.433	2.25	1.3761	0.8976	160	28.2	0.000
8.951	4.54	1.3790	0.9004	161	28.1	0.004
17.063	9.18	1.3891	0.9063	160	28.6	0.007
26.301	13.72	1.3983	0.9127	160	28.5	0.007

TABLE IV.

*Benzene Solutions.*

$p$	$n_D^{20}$	$n_D^{25}$	$d_4^{25}$	$V_{90}$ c.c.	$[\alpha]_D^{25}$ ( $c_0 = 1$ )	$[\alpha]_D^{25}$ ( $c_0 = 1$ )
0.9238	0.43	1.4995	0.8737	154	(26.6)	0.000
2.3214	1.24	1.4992	0.8747	159	30.5	0.004
4.586	2.36	1.4985	0.8765	160	29.3	0.000
11.348	5.78	1.4973	0.8813	161	28.8	0.004
16.940	8.59	1.4960	0.8864	161	28.6	0.048
22.455	11.30	1.4953	0.8909	161	28.2	0.041

The solvents used were not specially purified, but were prepared in such quantities that the same sample could be used throughout a series of experiments. The benzene and acetone were prepared from technical material by drying and fractional distillation. The following are the constants:

TABLE V.

Solvent	$n_D^{25}$	$n_D^{20}$
Alcohol .....	0.7878	1.3602
Acetone .....	0.7881	1.3571
Ethyl acetate .....	0.8947	1.3701
Benzene .....	0.8728	1.5004

The specific rotatory power of borneol is seen to depend only to a small extent on concentration or solvent; the expression  $(n^2 - 1)(n^2 + 1 + 1/a)$ , whilst varying with concentration in the same way as does  $[\alpha]$ , depends to a very great extent on the solvent, in the case of benzene which has its refractivity diminished by solution of borneol the expression has a sign opposite to that for the other solvents examined. Experiments now in progress show that this is not a general effect. Livens (*loc. cit.*) leaves it apparently an open question as to the dependence of  $a$  on the solvent. The results show that  $a$  decidedly depends on the nature of the solvent; there is no very apparent connexion between the value of  $a$  and the refractivity of the solvent.

that in which  $[\alpha]$  varies very little with concentration, the ratio  $(n^2-1)(n^2-1+1/a)$  also shows practically no variation, over the range of concentrations used the values of  $n^2-1$  and  $n^2+2$  vary considerably.

### Cinchonine.

was prepared according to Miller and Rohde's method (*Ber.*, 1906, 39, 1056). It was purified first by crystallisation of the base from water and then by crystallisation of the base from dry ether. Only sufficient was available for a limited examination.

TABLE VI.  
Alcohol Solutions.

	$n_D^{20}$	$n_D^{25}$	$d_4^{20}$	$d_4^{25}$	$[\alpha]_D^{20}$ (c = 1)	$[\alpha]_D^{25}$ (c = 1)
0.125	1.3607	1.3607	0.7887	75	50.5	0.413
0.59	1.3617	1.3617	0.7910	179	47.3	0.413
0.90	1.3630	1.3630	0.7920	222	47.2	0.411
2.67	1.3667	1.3667	0.7984	238	46.2	0.407
4.09	1.3695	1.3695	0.8032	243	45.8	0.404
7.69	1.3796	1.3796	0.8169	247	44.9	0.392
8.32	1.3800	1.3800	0.8186	259	44.2	0.390

TABLE VII.  
Acetone Solutions.

	$n_D^{20}$	$n_D^{25}$	$d_4^{20}$	$d_4^{25}$	$[\alpha]_D^{20}$ (c = 1)	$[\alpha]_D^{25}$ (c = 1)
0.58	1.3579	1.3579	0.7898	249	56.2	0.438
2.17	1.3614	1.3614	0.7951	244	50.2	0.435
4.05	1.3662	1.3662	0.8015	253	48.7	0.430
5.92	1.3711	1.3711	0.8100	238	49.0	0.425
8.60	1.3774	1.3774	0.8152	260	48.5	0.418

c = concentration in grams per 100 c.c.

Rapin (*Compt. rend.*, 1895, 120, 1170) gives  $[\alpha]_D^{20}$  in alcohol for cinchonine as  $48.25^\circ$ , but gives no account of a dependence on concentration. The above results show that in both alcohol and acetone  $[\alpha]$  decreases with increasing concentration. In both cases  $(n^2-1)(n^2-1+1/a)$  are very closely proportional; thus for the simple case of dependence on concentration Livers' suggestion, that the dependence is due simply to the variation in optical properties of the medium, seems to be true. If the dependence had been due to dynamic isomerism or a similar cause then  $[\alpha]$  and

$$(n^2-1)(n^2-1+1/a)$$

would not have varied together as has been explained in the Introduction.

For alcohol solutions the values of  $V_m$  increase with concentration. If this were a real and not an apparent phenomenon, it would be expected that the corresponding deformation of the molecule would lead to considerable variation in  $[\alpha]$ ; but deformation of the molecule would lead to a variation in  $n^2$  (see eq. (1)), and  $[\alpha]$  and  $(n^2 - 1)(n^2 + 1/a)$  would not vary together. In actual experiment they are very closely proportional. If variation in  $V_m$  is therefore probably, at least in part, due to alterations in the volume occupied by the alcohol. Thus by this method the effect of an active solute on the volume of a solvent can be at any rate qualitatively examined. Since at present there does not seem to be any mathematical basis for the mutual effects on density of solvent and solute, this method seems the only mode of attack; the theory of solutions in this respect lags far behind the optical theory.

Passing from alcohol to acetone both  $[\alpha]$  and

$$(n^2 - 1)(n^2 + 1/a)$$

increase. A reference to table X shows that  $a$  for these two solutions is approximately constant. In the case of acetone, however, the variation of  $[\alpha]$  with concentration is as great as for the alcohol solutions, the values of  $V_m$  for acetone solutions show such great dependence on concentration.

#### *Benzogluconic acid.*

Solutions of this substance were examined in order to see whether  $a$  or  $(n^2 - 1)(n^2 + 1/a)$  showed any constitutive effect.

TABLE VIII.

#### *Acetone Solutions.*

	$n_D$	$n_D$	$n_D$	$[\alpha]$	$V_m$ c.c. (g. 100 g. sol.)	$(n^2 - 1)(n^2 + 1/a)$
0.9448	0.735	1.3581	0.7916	38.9	322	0.80
2.5280	1.93	1.3623	0.7973	(38.2)	322	0.804
1.1584	3.25	1.3651	0.8033	39.1	322	0.804
6.2128	4.86	1.3726	0.8102	39.2	325	0.806

TABLE IX.

#### *Alcohol Solutions.*

	$n_D$	$n_D$	$n_D$	$[\alpha]$	$V_m$ c.c. (g. 100 g. sol.)	$(n^2 - 1)(n^2 + 1/a)$
0.9704	0.88	1.3621	0.7911	45.3	320	0.932
2.1028	1.80	1.3647	0.7954	42.8	320	0.930

TABLE X.

*Values of  $a$  for the Solutions Examined.*

Substance.	Solvent.	$a$ .	$1/a$ .
Cinchonine .....	Alcohol	0.747	1.337
" .....	Acetone	0.733	1.363
Benzoylcinchonine ...	Alcohol	1.006	0.994
" .....	Acetone	0.757	1.320
Quinid .....	Alcohol	0.468	2.132
" .....	Acetone	0.413	2.418
" .....	Ethyl acetate	0.515	1.938
" .....	Benzene	1.111	0.876

benzoylcinchonine shows a decrease in both  $[\alpha]$  and

$$(n^2 - 1)(n^2 - 1 + 1/a)$$

in passing from alcohol to acetone, the reverse of the case for cinchonine. There is no very apparent constitutive connexion even the value of  $a$  or  $(n^2 - 1)(n^2 - 1 + 1/a)$  for cinchonine and benzoyl derivative; both of these quantities depend too greatly on the nature of the solvent. However, the results obtained with acetone solutions confirm the interdependence of  $[\alpha]$  and  $(n^2 - 1)(n^2 - 1 + 1/a)$ . In passing from alcohol to acetone the values of  $[\alpha]$  for benzoylcinchonine decrease considerably, whilst the values of  $n_D^{20}$  show no very great variation.

For the cases examined in the present paper confirmation has been obtained of the theory that where variations in  $[\alpha]$  occur they are due to variations in the velocity of transmission of light within the medium, and not to causes directly affecting the degree of asymmetry of the molecule. It has, furthermore, been shown how  $[\alpha]$  can be obtained as to the effect of a solute on the density of a solvent.

Further work is in progress on these lines, and with the additional object of obtaining a value for the refractivity of an active substance.

In conclusion, the author wishes to express his thanks to the Messrs. Explosive Company, Ardeer Factory, and to Mr. W. J. G. F.I.C., Manager of the research section, for the facilities afforded for carrying out this work and permission to publish the results.

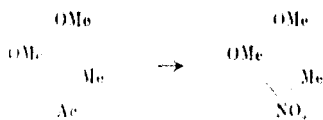
THE RESEARCH SECTION,  
MESSRS. EXPLOSIVES COMPANY,  
ARDEER.

CCLXII.—*Substitution in Aromatic Hydroxy-compounds. Part II. Acetyl-nitro-substitution.*

By VICTOR JOHN HARDING.

By the term acetyl-nitro substitution is meant the displacement of an acetyl group by a nitro-group. This displacement can be effected by the action of nitric acid on certain methoxyacetophenones, and it is believed to be direct, without the formation of any intermediate hydrogen substituted compound. So far as it has been studied, it is dependent on the presence of methoxy-groups on the benzene nucleus and on the position of the acetyl group. It is thought, however, that acetyl nitro substitution differs fundamentally from the substitution of a hydrogen atom by the nitro group (hydrogen nitro substitution), methoxy-groups merely enabling the nucleus to be more readily nitrated and thus giving an opening for the less mobile acetyl group to be substituted more easily than would otherwise have been the case.

The only instance in the literature of acetyl nitro substitution is the observation of Harding and Weizmann (T., 1910, **97**, 1155), who found that 4:5-dimethoxy-*o*-tolyl methyl ketone very readily gave 4-nitrohomocatechol dimethyl ether when treated with nitric acid:



The displacement of the aldehyde group by the nitro group (formyl nitro substitution) in aromatic methoxy-aldehydes, however, had been studied by Salway (T., 1909, **95**, 1155), who drew the conclusion that the displacement was direct.

The analogous case of the displacement of a carboxyl group by a nitro group (carboxyl nitro substitution) was discussed in the first of this series of communications (T., 1911, **99**, 1585). From a number of examples and the author's own experimental work, it was deduced that:

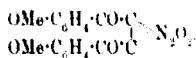
- (a) The substitution was direct, without the intermediate formation of the parent phenol ether.
- (b) The substitution took place only when the carboxyl group occupied a position which in the parent phenol ether was not towards nitric acid.

\* This communication is the second of a series on the subject of substitution in aromatic hydroxy-compounds.

is a study of the action of nitric acid on a series of methoxy ketones.

(a) *p*-Methoxyacetophenone,  $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{Me}$

The action of nitric acid on this ketone was first studied by Hermann, Ehrhardt, and Maisch (*Ber.*, 1890, **23**, 1202). The action of a mixture of concentrated sulphuric acid and nitric acid led to the formation of di 4-methoxybenzoylfuroxan (anisoyl furane peroxide):



On the other hand, Pope (P., 1912, **28**, 331) obtained the normal nitration product, 3-nitro-4-methoxyacetophenone.

Later result the author has confirmed, but by using nitric acid alone has obtained on two occasions the furoxan and at other times the nitro ketone.

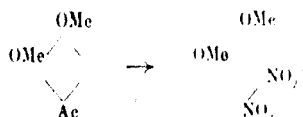
3-Nitro substitution does not take place in *p*-methoxyacetophenone and Salway (*loc. cit.*) failed to find any formyl nitro acetone during the nitration of anisaldehyde. The nitration of anisaldehyde, however, by a mixture of warm concentrated sulphuric and nitric acids results in carboxyl nitro substitution, a mixture of 2-nitroanisic acid and 2:4-dinitroanisole being obtained:



(see Cahours, *Annalen*, 1849, **69**, 236).

(b) 3:4-Dimethoxyacetophenone.

The action of nitric acid on this ketone does not appear to have been studied previously. In the cold or in warm glacial acetic acid formyl acetyl nitro substitution takes place very readily with the formation of 4:5-dinitroveratrole.



(c) 3:4:5-Trimethoxyacetophenone.

This ketone has previously been prepared by Maubner (*J. pr. Chem.*, 1910, [ii], **82**, 275) by the action of diazomethane on gall



## (d) 2:3:4-Trimethoxyacetophenone.

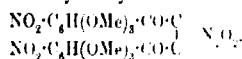
This well-known ketone has always been prepared by the methylation of 2-hydroxy-3:4-dimethoxyacetophenone (Perkin and Wilson, *J. Chem. Soc.*, 1902, **83**, 129; David and Kostanecki, *Ber.*, 1903, **36**, 2191; David and Schmid, *Ber.*, 1906, **39**, 214). Unsuccessful attempts were made to prepare it directly from the condensation of acetyl chloride and pyrogallol trimethyl ether through the agency of ferric chloride. Even although the reaction was only allowed to proceed a couple of hours and the temperature kept at 0°, the product of the reaction was always the hydroxy ketone, the methyl group in position 3 being hydrolysed. Using ferric chloride, however, as a condensing agent, partial success was attained. 2:4-Dimethoxyacetophenone was produced, although only in small amount, and its identity established by means of its benzylidene derivative.

Reaction of cold concentrated nitric acid on 2:3:4-trimethoxyacetophenone gives rise to 6-nitro-2:3:4-trimethoxyacetophenone:



Position 6, and not 5, is assigned to the nitro-group from the nitration reactions of nitric acid on pyrogallolcarboxylic acid trimethyl ether (Harding, T., 1911, **99**, 1585) and on its methyl ester (Knox and Goldstein, *Annalen*, 1907, **351**, 161).

The nitro-ketone, however, was isolated only as its piperonylidene derivative, and even that proved extremely difficult, and it is conceivable that in the oily nitration mixture which was used, 4-nitropyrogallol trimethyl ether might have existed and its presence remained undetected. In this way evidence of acetyl substitution might have been overlooked. In order to throw some light on this point, 2:3:4-trimethoxyacetophenone was treated to the vigorous action of warm nitric acid. If any 4-nitropyrogallol trimethyl ether had been produced in the less vigorous nitration it would certainly have shown itself in the more violent action as 4:5-dinitropyrogallol trimethyl ether (compare Knox and Siebeling, *Ber.*, 1911, **44**, 2115). No 4:5-dinitropyrogallol trimethyl ether was found, and the only product isolated from the vigorous nitration of 2:3:4-trimethoxyacetophenone was compared with which from its elementary analysis corresponded with 6-nitro-2:3:4-trimethoxybenzoylfuroxan:





Thus it will be seen that the evidence is quite against the presence of 4-nitropyrogallol trimethyl ether in the chief product of 2:3:4-trimethoxyacetophenone. Acetylation does not take place when the acetyl group occupies position in pyrogallol trimethyl ether. In this way acetyl-nitro-substitution is quite analogous to carboxyl-nitro-substitution. In neither does the substitution take place except when the acetyl or carboxyl group occupies a position which is active towards nitric acid in the parent phenol ether. The distribution of forces set up by methoxy groups determines the position entered by the nitro group, whether the group previously attacked be hydrogen, acetyl, or carboxyl. The corresponding case for the aldehyde group has yet been experimentally determined, although the author has no doubt that it will be found to follow the same rule.

In the next communication, which will follow shortly, will be given of a series of experiments on the action of nitric acid on a number of polymethoxy derivatives of benzene in the presence of carbamide and of hydrogen peroxide.

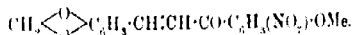
#### EXPERIMENTAL.

##### *Action of Nitric Acid on p-Methoxyacetophenone.*

Five grams of *p*-methoxyacetophenone were dissolved in 100 cc. of concentrated nitric acid and allowed to remain overnight, pouring into water an oily solid separated, which soon hardened and on being submitted to a process of fractional crystallization from alcohol proved to be entirely 3-nitro-4-methoxyacetophenone. No mono- or di-nitroanisole was found (Pope, P., 1912, 28).

In another experiment in which the time of reaction was fifteen minutes much unchanged ketone was recovered, and a small amount of di-*p*-methoxybenzoylfuroxan was isolated. The compound was identified by its melting point and analysis. The formation of any nitro-ketone was not observed, although the bulk of the recovered *p*-methoxyacetophenone was converted into a piperonylidene derivative and fractionally crystallized.

##### *3-Nitro-4-methoxyphenyl 3:4-Methylenebisstyryl Ketone*



This unsaturated ketone is readily obtained by combining 3-nitro-4-methoxyacetophenone and piperonal in alcoholic solution by a trace of potassium hydroxide. The ketone separates out from the alcoholic solution, and is purified by crystallization from glacial acetic acid, from which it separates in needles melting

Its solution in concentrated sulphuric acid is reddish-brown.

Calcd. gives 0.2979  $\text{CO}_2$  and 0.0501  $\text{H}_2\text{O}$ . C = 62.4; H = 4.2.

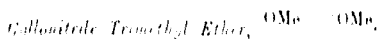
$\text{C}_{17}\text{H}_{15}\text{O}_6\text{N}$  requires C = 62.4; H = 4.0 per cent.

*Reaction of Nitric Acid on 3:4-Dimethoxyacetophenone. Formation of 4:5-Dinitroveratrole.*

A gram of 3:4-dimethoxyacetophenone was dissolved in 10 c.c. of concentrated nitric acid, and the reaction kept under control by means of running water. At the end of ten minutes the product was poured into water, and the yellow solid which separated was filtered and purified by crystallisation from alcohol. It crystallised in bright yellow needles, melting at 131–132°, and was found to be identical with 4:5-dinitroveratrole.

A gram of 3:4-dimethoxyacetophenone was dissolved in 10 c.c. of glacial acetic acid, 2 c.c. of concentrated nitric acid were added, and the solution was warmed. A vigorous reaction occurred, and when this had subsided the product was cooled and poured into water, when 4:5-dinitroveratrole separated and was easily identified

OMe



CN

This nitrile has previously been described by Helfer and Capellmann (*Ber.*, 1905, **38**, 3634), who obtained it by heating together a mixture of gallic acid trimethyl ether and lead thiocyanate.

It has also been described by Semmler (*Ber.*, 1908, **41**, 1918),

who prepared it by boiling oximinogallaldehyde trimethyl ether for 24 hours with acetic anhydride. The melting point is given as 93° by Helfer and Capellmann and 93° by Semmler. Gallonitrile

trimethyl ether is very readily and conveniently prepared from gallaldehyde trimethyl ether (Harding, T., 1911, **99**, 1593) by the

action of phosphorus pentachloride. The two substances were

used in equimolecular amounts in the presence of a little benzene,

refluxed together for a couple of hours in boiling water. The

benzene and phosphoryl chloride were then removed by distillation

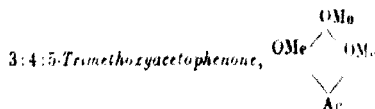
under diminished pressure. Any attempt, however, to distil the

residue at this stage resulted in decomposition, and therefore the

product was partly purified by crystallisation from aqueous alcohol. The nitrile was then distilled under diminished pressure, and

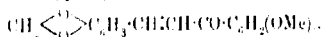
was purified by crystallisation from methyl alcohol. The melting

point was found to be 93°, and the yield 70 per cent. (Found, 93.2;  $\text{C}_{10}\text{H}_{11}\text{O}_3\text{N}$  requires N = 7.2 per cent.).



Three grams of magnesium and 15 grams of methyl iodide were converted into magnesium methyl iodide in ethereal solution. The greater part of the ether was removed by distillation, and a small amount of benzene added. A solution of gallionitrile (10 grams) in ether (20 grams) in benzene was then added, and the mixture allowed to continue for eighteen hours on a gently heated water bath. The yellow, insoluble product was decomposed by dilute hydrochloric acid. More ether was added, and the mixture solution extracted with a further quantity of ether. The ethereal extracts were washed with water, dilute sodium hydrochloric solution, and dilute aqueous potassium hydroxide in turn. The sodium carbonate washings were reserved (p. 2799). The organic extract was finally washed with dilute hydrochloric acid, and evaporated, and the residual oil fractionated under diminished pressure. The fractions of higher boiling point which were partly solid were then triturated two or three times with pure ether. This dissolved the ketone and a small amount of gallionitrile, which is almost insoluble in pure dry ether. The ethereal solution was filtered and evaporated, when the residue crystallised on keeping. The ketone crystallised from light petroleum in needles melting at 77–79° (Found, C = 62.6; H = 5.5. Calc., C = 62.8; H = 5.6 per cent.).

*3:4:5 Trimethoxyphenyl 3:4-Methylenedioxyethyl Ketone*



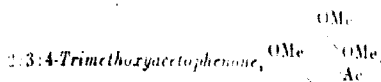
This derivative is prepared in an exactly similar manner to isomeric 2:3:4 trimethoxyphenyl 3:4-methylenedioxyethyl ketone (p. 2797). It crystallises from alcohol in bright yellow needles melting at 130–131°, and dissolves in concentrated sulphuric acid with a reddish violet coloration:

0.1179 gave 0.2907 CO<sub>2</sub> and 0.0583 H<sub>2</sub>O. C = 67.3; H = 5.5.  
C<sub>19</sub>H<sub>15</sub>O<sub>6</sub> requires C = 66.6; H = 5.5 per cent.

An oily *phenylhydrazine*, C<sub>17</sub>H<sub>15</sub>O<sub>3</sub>N<sub>2</sub>, was obtained by the condensation of 3:4:5 trimethoxyacetophenone and phenylhydrazine in acetic acid solution.

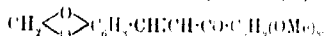
*Reaction of Nitric Acid on 3:4:5-Trimethoxyacetophenone:  
Formation of 5-Nitropyrogallol Trimethyl Ether.*

Half a gram of the ketone was dissolved in 2 c.c. of warm acetic acid, and 0.5 c.c. of concentrated nitric acid added. There was an instantaneous reaction, and the product was heated in a water-bath until the copious evolution of nitrous fumes had ceased. On cooling and pouring into water, 5-nitropyrogallol trimethyl ether was precipitated, and was readily identified by its crystalline form (from alcohol) and its melting point. When compared with a specimen of 5-nitropyrogallol trimethyl ether prepared from pyrogallol trimethyl ether the melting point remained unaltered.



Four grams of pyrogallol trimethyl ether and 9 grams of ferric chloride were dissolved in carbon disulphide, 15 grams of sulphuric acid as ferric chloride added, and the reaction was allowed to continue overnight. The black product was decomposed by ice and dilute hydrochloric acid, the carbon disulphide removed by distillation under a current of steam, and the residual, dark coloured, only extracted by means of ether. The ethereal extract was washed with dilute potassium hydroxide, which removed much 2-hydroxy-3-methoxyacetophenone, dried, and distilled, when an oil boiled at 106–127° passed over. This was identified by analysis:  $\text{C}=62.7$ ;  $\text{H}=6.6$ ;  $\text{C}_{11}\text{H}_{11}\text{O}_4$  requires  $\text{C}=62.8$ ;  $\text{H}=6.6$  per cent. and by its piperonylidene derivative as 2:3:4-trimethoxyacetophenone.

*3:4:5-Trimethoxyphenyl 3:4-Methylenedioxybenzyl Ketone,*



This derivative was prepared by mixing equimolecular amounts of benzal and 2:3:4-trimethoxyacetophenone in alcoholic solution and condensing them by means of a few drops of 50 per cent. aqueous potassium hydroxide and boiling. The product was cooled, water added, and the piperonylidene compound separated as an oily solid, which rapidly hardened. It crystallises from alcohol in stout needles, melting at 101–102°, and dissolves in concentrated sulphuric acid with a deep red colour:

Analysis gave 0.2953  $\text{CO}_2$  and 0.0594  $\text{H}_2\text{O}$ .  $\text{C}=66.9$ ;  $\text{H}=5.5$ .

$\text{C}_{19}\text{H}_{15}\text{O}_6$  requires  $\text{C}=66.6$ ;  $\text{H}=5.5$  per cent.

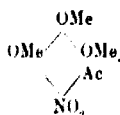
Found,

S. G.

The same piperonylidene derivative is obtained by the condensation of piperonal with 2:3:4-trimethoxyacetophenone either by the direct condensation of acetyl chloride and trimethyl ether through the agency of ferric chloride, or by the methylation of 2-hydroxy-3:4-dimethoxyacetophenone (compare Perkin and Wilson, T., 1903, **83**, 129).

*Action of Nitric Acid on 2:3:4-Trimethoxyacetophenone*

(a) *Formation of 6(3) Nitro-2:3:4-trimethoxyacetophenone*



Two grams of 2:3:4-trimethoxyacetophenone were dissolved in concentrated nitric acid, and the solution was kept cold for five minutes by immersion in running water. There was no visible reaction, and at the end of that time the solution was diluted with much water, when a heavy oil separated, which did not solidify on keeping. In order to determine whether this oil consisted of unchanged 2:3:4-trimethoxyacetophenone or a nitro-substance, it was converted into its piperonylidene derivative. The oil was extracted by means of ether, the ethereal solution washed with dilute sodium carbonate solution, dried, and evaporated. The residual oil was dissolved in boiling alcohol, a considerable excess of piperonal added, and a few drops of aqueous potassium hydroxide. Condensation took place readily, the piperonylidene compound separating as a red oil, which could not be obtained in solid condition. The alcoholic solution was diluted with water, and the whole of the red oil which separated was extracted by means of ether. The ethereal solution was then washed several times with a concentrated solution of sodium hydrogen sulphate to remove the excess of piperonal, dried, and evaporated. This residue was almost insoluble in cold alcohol, but dissolved readily in boiling solvent, which, on cooling, deposited the piperonylidene compound as an oil. By exposure to a temperature of about 10° for more than a week, however, the oil solidified, and a pure compound solid was obtained, which crystallised from alcohol and melted at 96-97° to a deep yellow liquid. The almost colourless solid, however, always contained some of a deep yellow colour, but on several crystallisations the whole changed into a deep yellow solid. This melted at 111-112°, dissolved in concentrated sulphuric acid with a reddish-yellow colour, and evidently

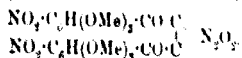
gave 4:6-nitro-2:3:4-trimethoxyphenyl-3:4-methylenedioxyethyl acetate.

0.158 gave 0.2541  $\text{CO}_2$  and 0.0432  $\text{H}_2\text{O}$ .  $\text{C} = 58.4$ ;  $\text{H} = 4.0$ .

0.749 „ 7.2 c.c.  $\text{N}_2$  (moist) at  $25^\circ$  and 758 mm.  $\text{N} = 4.5$ .

$\text{C}_{15}\text{H}_{12}\text{O}_8\text{N}_2$  requires  $\text{C} = 58.9$ ;  $\text{H} = 4.3$ ;  $\text{N} = 5.6$  per cent.

*Formation of Di-6-nitro-2:3:4-trimethoxybenzoyltartronic.*



The action of hot concentrated nitric acid on 2:3:4-trimethoxyphenone was investigated in the hope that acetyl substitution would occur, and as a result that 4:5-dinitropyrogallol trimethyl ether would be isolated. One gram of 2:3:4-trimethoxyacetophenone was dissolved in concentrated nitric acid and the solution stood until the vigorous reaction, which had set in, ceased. The mixture was diluted with water, when a slightly oily solid was precipitated. The water was decanted, and on adding alcohol the residue became completely solid. It was collected and purified by crystallisation from benzene, from which it separated in small, dirty yellow needles:

0.1217 gave 0.2098  $\text{CO}_2$  and 0.0413  $\text{H}_2\text{O}$ .  $\text{C} = 47.0$ ;  $\text{H} = 3.7$ .

$\text{C}_{12}\text{H}_8\text{O}_{11}\text{N}_4$  requires  $\text{C} = 46.9$ ;  $\text{H} = 3.5$  per cent.

Di-6-nitro-2:3:4-trimethoxybenzoyltartronic is insoluble in water, alcohol, or dilute sodium carbonate, but dissolves in hot acetic acid. No 4:5-dinitropyrogallol trimethyl ether was isolated from either liquors.

*Isolation of a Compound,  $\text{C}_{21}\text{H}_{12}\text{O}_8\text{N}_4$ , from the Action of Methyl Iodide on Gallonitrile Trimethyl Ether* (p. 2795).

The sodium carbonate washings from the Grignard reaction (p. 2796) were evaporated on the water bath for a short time to remove the ether, cooled, and 50 per cent. aqueous potassium cyanide was added until no more precipitate appeared. The precipitated potassium salt was collected, suspended in warm water, and decomposed by dilute hydrochloric acid, when an oil was precipitated which solidified on cooling. The solid was collected and purified by crystallisation from benzene, from which it separated in small prisms melting at  $125-126^\circ$ :

0.136 gave 0.2773  $\text{CO}_2$  and 0.0564  $\text{H}_2\text{O}$ .  $\text{C} = 61.1$ ;  $\text{H} = 5.1$ .

$\text{N}_2$  required 11.6 c.c.  $\text{N} = 10\text{H}_2\text{SO}_4$ .  $\text{N} = 6.6$ .

$\text{C}_{21}\text{H}_{12}\text{O}_8\text{N}_4$  requires  $\text{C} = 60.9$ ;  $\text{H} = 5.3$ ;  $\text{N} = 6.7$  per cent.

$\text{C}_{21}\text{H}_{12}\text{O}_8\text{N}_4$  „ „  $\text{C} = 61.1$ ;  $\text{H} = 4.9$ ;  $\text{N} = 6.8$  „ „ „

\* Other analyses gave  $\text{C} = 61.2$ ;  $\text{H} = 5.2$ ;  $\text{N} = 6.5$ .

It was found that a determination of the basicity of the acid by titration with normal alkali gave untrustworthy results, the end-point with phenolphthalein being extremely indefinite.

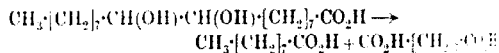
In conclusion, I desire to thank the Research Fund Committee of the Chemical Society for the grant which has defrayed part of the cost of this investigation.

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MONTREAL.

CCCLXIII.—*The Mechanism of the Action of Fused Alkalis. Part I. The Action of Fused Potassium Hydroxide on Dihydroxystearic Acid and Dihydroxybenic Acid.*

By HENRY RONDEL LE SUEUR and JOHN CHARLES WITHERS.

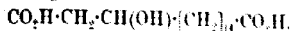
ONE of the stages in a method for the determination of the constitution of fatty acids (Crossley and Le Sueur, T., 1899, **75**, 12; 1900, **76**, 83) consists in the oxidation of the dihydroxy derivative of the acid under investigation by means of chromic acid, and it was pointed out at the time that when dealing with a higher fatty acid the insolubility of its hydroxylated derivative might render this oxidation a difficult operation. It was thought that perhaps the hydroxylated derivative with potassium hydroxide might replace the oxidation with chromic acid, and in order to investigate this point one of us (Le Sueur, T., 1901, **79**, 131a) fused dihydroxystearic acid with potassium hydroxide in the hope that oxidation would take place thus:



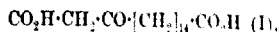
The results obtained, however, were quite different, and it was shown that the main product of the action was a monohydroxy dicarboxylic acid of the formula  $\text{C}_{18}\text{H}_{34}\text{O}_5$ . The present investigation deals with the constitution of this acid and also of a similar acid obtained by the fusion of dihydroxybenic acid with potassium hydroxide.

When the acid  $\text{C}_{18}\text{H}_{34}\text{O}_5$  is oxidised with potassium permanganate in acetone solution it is quantitatively converted into a tetracarboxylic acid having the formula  $\text{C}_{17}\text{H}_{32}\text{O}_8$ ; and when it is heated

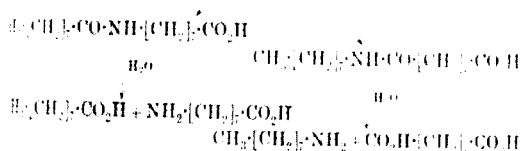
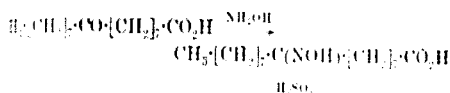
above and above its melting point it readily loses water and two *trans*-unsaturated dicarboxylic acids,  $C_{18}H_{32}O_4$ , are produced. These facts led us to suppose that the acid  $C_{18}H_{34}O_5$  was a hydroxy-acid having the constitution



such an acid would give on oxidation the ketonic acid,



the latter would readily lose carbon dioxide to give the acid,  $CH_3 \cdot CO \cdot (CH_2)_{14} \cdot CO_2H$ . Although the free acid (I) possibly could not be isolated, one would expect that its ethyl ester would be sufficiently stable to admit of this being done. We accordingly prepared the ethyl ester of the acid,  $C_{18}H_{34}O_5$ , with oxidising agents, but in spite of a large number of experiments we were unable to obtain the desired ester; either no oxidation took place or if it did, carbon dioxide was lost simultaneously, and the acid  $C_{17}H_{32}O_5$  was produced. We then decided to determine the constitution of the ketonic acid, and for this purpose it was treated with hydroxylamine, and the resulting oxime converted into the corresponding amide by heating with concentrated sulphuric acid, and these amides were hydrolysed by heating with hydrochloric acid. The products of the hydrolysis were identified as *n*-nonoic acid, octylamine, azelaic acid, and  $\gamma$ -amino-octoic acid. From this it follows that the ketonic group is in the middle of the chain, and that the above products are formed as follows:

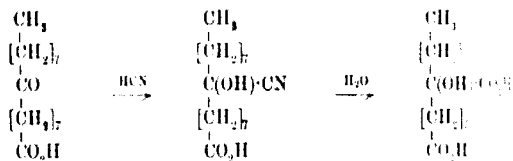


The position of the carbonyl group and, of course, of the  $CH \cdot OH$  group which gives rise to it, having been established, it now remained to determine the position of the carboxyl group which is introduced in the formation of the ketonic acid by the oxidation of the acid  $C_{18}H_{34}O_5$ . It was natural to suppose that it was at the



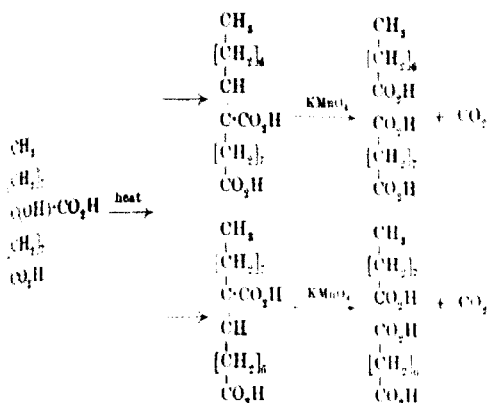
end of the chain, and that the constitution of the acid  $C_{17}H_{32}O_4$  was  $CO_2H \cdot [CH_2]_7 \cdot CH(OH) \cdot [CH_2]_7 \cdot CO_2H$ . The loss of water when such an acid is heated and of carbon dioxide when it is oxidized are difficult to explain, and this difficulty led us to investigate further.

It has been stated already that when the acid  $C_{18}H_{34}O_4$  is heated above its melting point it readily loses water to give the unsaturated acids  $C_{18}H_{32}O_4$ , and on submitting these to oxidation *separately* along the chain the following acids were obtained: *n*-octoic, *n*-heptadecanoic, suberic, and azelaic. The occurrence of azelaic acid in the oxidation products shows that the group  $\cdot C \cdot [CH_2]_7 \cdot C \cdot$  is present in the parent acid, and the formation of *n*-nonoic acid under similar conditions is evidence that the group  $CH_3 \cdot [CH_2]_7 \cdot C \cdot$  is also present. These results point to the conclusion that one of the carboxyl groups in the acid  $C_{18}H_{34}O_4$  is near the middle of the chain, and this is supported by the fact that when the unsaturated acids formed by the loss of water from the acid  $C_{18}H_{34}O_4$  are reduced with hydrogen in the presence of platinum black a saturated dicarboxylic acid,  $C_{17}H_{34}O_4$ , melting at  $71.5-72.5^\circ$ , is obtained, whereas the normal dicarboxylic acid,  $CO_2H \cdot [CH_2]_{16} \cdot CO_2H$ , melts at  $118^\circ$ . This and other considerations led us to the conclusion that one of the carboxyl groups and a hydroxyl group were attached to one and the same carbon atom, and that the acid  $C_{18}H_{34}O_4$  was  $\alpha$ -hydroxy  $\alpha$ -octyl-octanoic acid,  $CH_3 \cdot [CH_2]_7 \cdot C(OH)(CO_2H) \cdot [CH_2]_7 \cdot CO_2H$ . This was proved correct beyond all doubt by the actual synthesis of the acid by the means of the hydrogen cyanide method thus:



The synthetic acid had all the properties of the original acid, thus when oxidized with potassium permanganate it gave the ketonic acid  $C_{17}H_{32}O_3$ , melting at  $78.5^\circ$ , and when heated it readily lost water to give a product which readily reduced potassium permanganate, etc.

The identification of *n*-octoic acid, *n*-nonoic acid, suberic, and azelaic acid as the products of the oxidation by potassium permanganate of the unsaturated acids produced by the removal of the elements of water by heat from  $\alpha$ -hydroxy  $\alpha$ -octyl-octanoic acid shows that this loss takes place in two directions thus

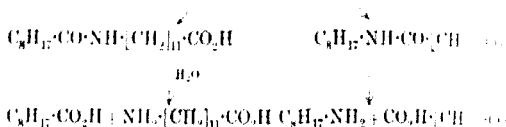
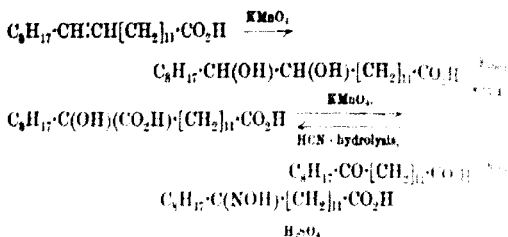


the product of the fusion of dihydroxystearic acid with potassium hydroxide also contains small quantities of a second acid, which we find to be identical in all respects with the ketonic acid,  $\text{H}_2\text{O}$ , melting at  $78.5^\circ$ , and produced by the oxidation of the  $\text{C}_{15}\text{H}_{34}\text{O}_4$  with potassium permanganate. That the occurrence of a ketonic acid amongst the products of the fusion is due to a further oxidation of the acid  $\text{C}_{15}\text{H}_{34}\text{O}_4$ , is proved by the fact that it is formed when the acid  $\text{C}_{15}\text{H}_{34}\text{O}_4$  itself is fused with sodium hydroxide.

In the previous communication (T., 1901, **79**, 1313) dealing with the fusion of dihydroxystearic acid with potassium hydroxide the acid  $\text{C}_{15}\text{H}_{34}\text{O}_3$  was erroneously assigned to this second acid amongst the products of the fusion. This error is easily explained for when one remembers that the amount of this acid isolated at that time was small, and that there is only a small difference between the percentages of carbon and hydrogen required for the formula  $\text{C}_{15}\text{H}_{34}\text{O}_3$  and  $\text{C}_{17}\text{H}_{36}\text{O}_3$ .

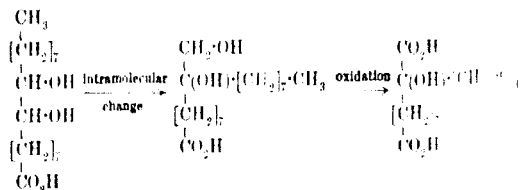
In order to see how far this remarkable reaction was general we carried out a similar investigation of the action of fused potassium hydroxide on dihydroxybenzoic acid, and find that the reaction in this case is exactly analogous to that with dihydroxystearic acid. Dihydroxybenzoic acid, obtained by the oxidation of erucic acid with potassium permanganate in alkaline solution, when fused with potassium hydroxide is converted into the monohydroxybenzoic acid,  $\text{C}_{22}\text{H}_{20}\text{O}_3$ , which on oxidation with potassium permanganate loses carbon dioxide, and yields the ketonic acid,  $\text{H}_2\text{O}$ . The constitution of this ketonic acid has been deter-

mined, and the parent acid synthesised from it by the cyanide method. These various changes are tabulated below.



The product of the fusion of dihydroxybehenic acid with potassium hydroxide also contains small quantities of the ketone  $\text{C}_{21}\text{H}_{40}\text{O}_2$ , which is undoubtedly formed by the oxidation of the acid  $\text{C}_{22}\text{H}_{42}\text{O}_3$  by the fused potassium hydroxide.

The above intramolecular changes which take place during fusion with potassium hydroxide are of particular interest, as they involve the migration of the heavy group  $\text{C}_8\text{H}_{17}$  from one carbon atom to another adjacent to it. It is probable that this change precedes oxidation, and that an acid containing a primary alcohol group is formed as an intermediate product. If this assumption is granted, then the formation of the dicarboxylic acid can be explained, for it has been shown that primary alcohols do not yield acids when they are fused with potassium hydroxide (Guerbet, *Compt. rend.*, 1911, **153**, 1487; 1912, **154**, 222, 713):



with the object of obtaining direct evidence as to the correctness of the above supposition we fused dihydroxystearic acid with potassium hydroxide in an atmosphere of nitrogen, and in this way hoped to limit the reaction to the intramolecular change. In this, however, we were not successful, as the product under these conditions is also the acid  $C_{15}H_{34}O_4$ , the yield of acid being the same in both cases. This result is nevertheless interesting as it shows that the oxidation occurring during the fusion is not dependent on the presence of atmospheric oxygen.

We have been unable to find any record of the movement of such a heavy group within the molecule of an aliphatic compound. A somewhat analogous case in the aromatic series is the formation of benzoic acid by the action of fused potassium hydroxide on benzoin and by the action of aqueous potassium hydroxide and air on benzoin.

#### EXPERIMENTAL.

##### *Preparation of $\alpha$ -Hydroxy $\alpha$ -octylsuccinic Acid,*



The acid was obtained by the fusion of dihydroxystearic acid with potassium hydroxide, and the method employed did not differ in essential detail from that described in a previous communication (Le Sueur, T., 1901, **79**, 1317), except that the acid formed by acidifying the aqueous solution of the fusion was washed in ether, the ethereal solution dried and evaporated, and the residue crystallised from a mixture of benzene and chloroform. The yield of pure acid melting at 111–112° was very constant, amounted to 65 per cent. of the theoretical.

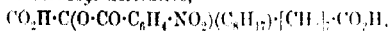
The benzoyl derivative,  $CO_2H \cdot C(OBz)(C_8H_{17}) \cdot [CH_2]_7 \cdot CO_2H$ , was prepared by the Schotten-Baumann method, in the hope of obtaining a solid derivative which would serve to characterise the parent acid. Unfortunately, it proved to be a glassy mass, which could not be purified:

0.369 gave 0.5776  $CO_2$  and 0.1838  $H_2O$ . C = 68.22; H = 8.91.

0.339 required 15.9 c.c. 0.1N-NaOH. M.W. = 432.6.

$C_{27}H_{50}O_4$  requires C = 69.08; H = 8.82 per cent. M.W. = 434.3.

The *m*-nitrobenzoyl derivative,



was prepared from the acid and *m*-nitrobenzoyl chloride by the Schotten-Baumann method. The product was a viscid mass, which, after treatment with dilute hydrochloric acid, was freed from benzoic acid by boiling with water. The insoluble residue was crystallised, first from dilute formic acid and then from a mixture of chloroform and light petroleum, from which it separates as a

white powder melting at 80–81°. It is insoluble in light petroleum, and soluble in chloroform or glacial formic acid.

0.2078 gave 5.4 c.c.  $N_2$  at 22° and 755 mm.  $N = 2.91$

$C_{17}H_{31}O_3N$  requires  $N = 2.92$  per cent.

*Preparation of  $\theta$ -Ketomargaric Acid,  $C_{17}H_{31}CO(CH_2)_7CO_2H$*

Ten grams of  $\alpha$ -hydroxy- $\alpha$ -octylsebacic acid were dissolved in 160 c.c. of acetone (previously purified by treatment with potassium permanganate) and 20 c.c. of water, and the mixture was gradually warmed with powdered potassium permanganate, which was gradually added. After the addition of 8 grams of permanganate, oxidation proceeded very slowly. The acetone was then removed by distillation, the residue treated with water, and the manganese dioxide dissolved by dilute sulphuric acid and sulphur dioxide. The precipitated acid was dissolved in ether, the ethereal solution washed, dried, evaporated, and the residue crystallised from a mixture of chloroform and light petroleum. The yield was 7.5 per cent. of the theoretical:

0.1560 gave 0.4098  $CO_2$  and 0.1578  $H_2O$ .  $C = 71.64$ ;  $H = 11.35$

0.3766 required 13.6 c.c. 0.1N-NaOH. M.W. = 277.

$C_{17}H_{32}O_2$  requires  $C = 71.77$ ;  $H = 11.35$  per cent. M.W. = 276.

$\theta$ -Ketomargaric acid,  $C_{17}H_{31}CO(CH_2)_7CO_2H$ , is readily soluble in cold chloroform and moderately so in ether, alcohol, or acetate, or benzene in the cold. It is insoluble in light petroleum and crystallises from a mixture of this solvent and chloroform in glistening plates melting at 78.5°. It is not oxidised by an acid solution of potassium permanganate in the cold. The acid is produced by the fusion with potassium hydroxide of any  $\alpha$ -hydroxy- $\alpha$ -octylsebacic acid. The white *silver* salt was obtained on diluting a warm alcoholic solution of the sodium salt of the acid to a cold alcoholic solution of silver nitrate:

0.2784 gave 0.0784 Ag. Ag = 28.16.

$C_{17}H_{31}O_3Ag$  requires Ag = 27.60 per cent.

*Methyl  $\theta$ -ketomargarate,  $C_{17}H_{31}CO(CH_2)_7CO_2Me$ , was obtained by heating for four and a-half hours on the water-bath a mixture of 8.5 grams of the acid, 90 c.c. of methyl alcohol, and 45 c.c. concentrated sulphuric acid. The product was poured into cold water, the ester dissolved in ether, the ethereal solution dried, evaporated, and the residue crystallised from methyl alcohol, from which it separates in large, pearly flakes, melting at 45.5°:*

0.1518 gave 0.4030  $CO_2$  and 0.1585  $H_2O$ .  $C = 72.40$ ;  $H = 11.49$

$C_{18}H_{34}O_2$  requires  $C = 72.42$ ;  $H = 11.49$  per cent.

\* A second analysis gave  $C = 71.69$ ;  $H = 11.40$ .

*β-ketomargarate*,  $C_{17}H_{33}O_5 \cdot CO \cdot (CH_2)_4 \cdot CO \cdot Et$ , was prepared by the method used for the preparation of the methyl ester, and was purified by crystallisation from dilute alcohol, from which it separates in pearly flakes melting at  $38^\circ$ . It is readily soluble in alcohol, benzene, chloroform, or acetone in the cold.

0.160 gave 0.2964  $CO_2$  and 0.1172  $H_2O$ .  $C = 72.89$ ;  $H = 11.83$ .

$C_{19}H_{35}O_5$  requires  $C = 73.01$ ;  $H = 11.62$  per cent.

*β-ketomargaramide*,  $C_{17}H_{31}O_5 \cdot CO \cdot (CH_2)_4 \cdot CO \cdot NH_2$ , was prepared by heating 12 grams of the ketonic acid and 0.8 gram of thionyl chloride were heated together on the water bath for half an hour, and the cold product was poured into excess of ammonia. The precipitated amide was dissolved in ether, the solution washed, and then evaporated, and the residue crystallised from a mixture of chloroform and light petroleum, when it was obtained in needles melting at  $119^\circ$ . It is insoluble in light petroleum, but dissolves in alcohol, chloroform, ether, benzene, or hot water.

0.160 gave 4.6 c.c.  $N_2$  at  $21^\circ$  and 762 mm.  $N = 4.75$ .

$C_{17}H_{31}O_5N$  requires  $N = 4.95$  per cent.

*β-ketomargaranilide*,  $C_{17}H_{31}O_5 \cdot CO \cdot (CH_2)_4 \cdot CO \cdot NHPh$ , was obtained by the action of the acid chloride (prepared by the interaction of acid and thionyl chloride) on aniline. It was purified by crystallisation, first from acetic acid and then from formic acid, and was obtained as a white, crystalline powder, melting at  $96.5^\circ$ . It dissolves freely in alcohol, acetone, chloroform, or benzene, is sparingly soluble in ether, acetic acid, or formic acid in the cold, and is insoluble in light petroleum.

0.225 gave 9.9 c.c.  $N_2$  at  $19^\circ$  and 770 mm.  $N = 3.95$ .

$C_{23}H_{35}O_5N$  requires  $N = 3.90$  per cent.

The *semicarbazone* of *β-ketomargaric acid* was obtained by heating for five hours on the water bath an aqueous alcoholic solution of 0.6 gram of the acid, 0.5 gram of semicarbazide hydrochloride, and 0.5 gram of dry potassium acetate, and was purified by crystallisation from acetone, from which it separates in stellar aggregates of prisms melting at  $111^\circ$ . It is sparingly soluble in alcohol, acetone, or ethyl acetate in the cold, and is insoluble in ether or light petroleum.

0.1206 gave 13.1 c.c.  $N_2$  at  $19^\circ$  and 774 mm.  $N = 12.55$ .

$C_{18}H_{31}O_5N_3$  requires  $N = 12.31$  per cent.

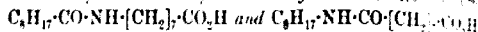
The *oxime* of *β-ketomargaric acid* was prepared by boiling on the water bath for three hours a solution of 5 grams of the acid, 2 grams of hydroxylamine hydrochloride, and 3 grams of sodium acetate in a mixture of 10 c.c. of alcohol and 20 c.c. of water. The alcohol was then evaporated, and the product poured into

dilute sulphuric acid, when the precipitated oil was extracted with ether. The ethereal solution was washed with water, dried, and evaporated. The residue was a colourless oil, which did not solidify even on leaving in a vacuum desiccator for three months.

0.2618 gave 9.8 c.c.  $N_2$  at  $15^\circ$  and 750 mm.  $N=4.30$ .

$C_{17}H_{33}O_3N$  requires  $N=4.68$  per cent.

*Conversion of the Oxime of  $\theta$ -Ketomargaric Acid into the Amides*



The oxime (8 grams) was slowly poured into concentrated sulphuric acid (40 c.c.) and the solution heated for one and a half hours on the water-bath. The resulting dark brown liquid was cooled and slowly poured on crushed ice, and the precipitated amides were collected and crystallised from dilute acetic acid, from which they separated in aggregates of thin plates melting at  $68.5-69.5^\circ$ . Although the substance thus isolated is undoubtedly a mixture of two amides, its melting point is nevertheless very sharp:

0.2450 gave 10.4 c.c.  $N_2$  at  $17.5^\circ$  and 758 mm.  $N=4.26$ .

$C_{17}H_{33}O_3N$  requires  $N=4.68$  per cent.

*Hydrolysis of the above Amides.*—2.5 Grams of the amides were heated with 12 c.c. of concentrated hydrochloric acid in a test-tube at  $180^\circ$  for four hours. The dark brown products from several such quantities were mixed with water and distilled in a current of steam (distillate=A). The residue was then made alkaline and again distilled in steam (distillate=B). The residue was now concentrated to a small bulk, and poured into excess concentrated hydrochloric acid, and the mixture left for some time when a crystalline solid separated (solid=C), which was removed by filtration (filtrate=D).

*Distillate A* was extracted several times with much ether, the ethereal solution washed twice with small quantities of water, dried, and evaporated. The residue obtained from 21 grams of the mixed amides weighed 4.8 grams, and all distilled between  $248^\circ$  and  $255^\circ$ ; it was purified by fractional distillation, a 10-portion boiling at  $251-253^\circ$  collected for analysis. This fraction readily solidified on cooling in ice, and the resulting solid melted at  $12-13^\circ$ :

0.3120 required 21.6 c.c. 0.1N NaOH. M.W. = 158.4.

*n* Nononic acid,  $C_9H_{19}O_2$ , has M.W. = 158, b. p.  $253-4^\circ$  (corr.) (m. p.  $12.6^\circ$ ). The identity of the acid with *n* nononic acid is further proved by converting a small quantity of it into the

which, after crystallisation from absolute alcohol, melted at  $174^{\circ}$ , which is the melting point of zinc succinate.

*Residue B.*—This alkaline distillate was acidified with hydrochloric acid, the resulting solution mixed with much ether in a separating funnel, and then made strongly alkaline with potassium peroxide, and the whole quickly shaken. This procedure was repeated in order to enable the ether to dissolve the base before the water had time to combine with the water to form a hydrate. The dried ethereal solution on evaporation gave a residue which melted between  $173^{\circ}$  and  $177^{\circ}$ . A small quantity of this was converted into the platinichloride, which was analysed (Found, Pt=29.15.  $[\text{C}_8\text{H}_{17}\cdot\text{NH}_2\cdot\text{HCl}]_2\cdot\text{PtCl}_4$  requires Pt=29.21 per cent.).

The free base gave the carbylamine reaction, and readily absorbed carbon dioxide from the air. It is therefore identical with octylamine, the boiling point of which is  $175^{\circ}$ – $177^{\circ}$ .

*Phenyl-octylcarbamide*,  $\text{C}_8\text{H}_{17}\cdot\text{NH}\cdot\text{CO}\cdot\text{NHPh}$ , was prepared by mixing 0.4 gram (1 mol.) of phenylcarbimide to 0.4 gram (1 mol.) of the above base, dissolved in 10 c.c. of dry benzene, and allowing the mixture to remain overnight. The solution was then concentrated to half its bulk, and mixed with light petroleum. The residue which separated was dissolved in a mixture of benzene and light petroleum, from which it crystallises in flakes, melting at  $158^{\circ}$ . It is readily soluble in alcohol, chloroform, or benzene, and is insoluble in light petroleum:

1588 gave 17.4 c.c.  $\text{N}_2$  at  $19^{\circ}$  and 776 mm. N=11.32.

$\text{C}_{15}\text{H}_{21}\text{ON}_2$  requires N=11.29 per cent.

*Substance C.*—This consisted of long, flat needles, melting at  $106.5^{\circ}$ , which, after crystallisation from water, were quite colourless and melted at  $106.5^{\circ}$ . The acid had the characteristic appearance of azelaic acid (m. p.  $106^{\circ}$ ), with which it is undoubtedly identical (Found, C=57.40; H=8.75. M.W. 189.6.  $\text{H}_2\text{O}$  requires C=57.40; H=8.58 per cent. M.W. 188).

*Residue D.*—This, which contained much free hydrochloric acid, was evaporated to dryness, the residue partly dried, and then repeatedly extracted with acetone. This acetone solution on evaporation left a residue which was dissolved in hot alcohol, and the resulting solution was mixed with an equal volume of ether. From the mixture the hydrochloride of the amino acid was deposited gradually in glistening needles melting at  $145^{\circ}$ – $146^{\circ}$ . (The hydrochloride of  $\gamma$ -amino-*n*-octoic acid melts at  $147^{\circ}$ ). (Found, N=7.10.  $\text{H}_2\text{O}\cdot\text{N}\cdot\text{HCl}$  requires N=7.16 per cent.) A small quantity of the hydrochloride was converted into the platinichloride (Found, Pt=26.69. Calc., Pt=26.80 per cent.).



The amino acid resulting from the hydrolysis of the  $\beta$ -lactam is, therefore,  $\gamma$ -amino- $\alpha$ -octoic acid.

The yields of the four substances obtained by the hydrolysis of the mixed amides were as follows:

$\alpha$ -Nonoic acid .....	85.4 per cent. of theoretical
Octylamine .....	86.5 " "
Azelic acid .....	83.0 " "
Hydrochloride of $\gamma$ -amino- $\alpha$ -octoic acid ..	67.0 " "

*Formation of the Unsaturated Acids,  $C_{13}H_{22}O_4$ , from  $\alpha$ -Hydroxy- $\alpha$ -octylsebacic Acid.*

Eight grams of  $\alpha$ -hydroxy- $\alpha$ -octylsebacic acid were placed in a flask heated under a pressure of 25 mm. in a distilling flask placed in a metal bath. Effervescence, due to the evolution of  $CO_2$  vapour, began at about  $220^\circ$ , and rapidly increased as the temperature rose. The vapour evolved contained only a trace of  $SO_2$  dioxide. The temperature was maintained at about  $280^\circ$  until effervescence had ceased, and then raised gradually, when liquid distilled between  $290^\circ$  and  $310^\circ$  and gave 6.8 gram distillate. This was redistilled under 30 mm. pressure, a portion boiling at  $294^\circ$ – $295^\circ$  collected for analysis:

0.1624 gave 0.4152  $CO_2$  and 0.1520  $H_2O$ .  $C = 69.72$ ;  $H = 10.258$ .  
 $C_{13}H_{22}O_4$  requires  $C = 69.23$ ;  $H = 10.258$  per cent.

A specimen from another preparation was converted into silver salt and analysed:

0.2168 gave 0.0870 Ag.  $Ag = 40.13$ .  
 $C_{13}H_{20}O_4Ag_2$  requires  $Ag = 41.02$  per cent.

The above figures agree sufficiently with the calculated values to show that the substance is produced from  $\alpha$ -hydroxy- $\alpha$ -octylsebacic acid by the loss of water only. It was kept for several days but could not be obtained as a definite solid; also, redistillation under diminished pressure produced slight decomposition. Elimination of water from  $\alpha$ -hydroxy- $\alpha$ -octylsebacic acid by heating it with sulphuric acid was also tried. For this purpose the acid was heated at  $200^\circ$ – $220^\circ$  for four and a half hours with 5 per cent. sulphuric acid in a sealed tube. Much sulphur dioxide evolved when the tube was opened, and the contents were found to consist for the most part of  $\beta$ -ketomargaric acid, melting at  $78.5^\circ$ . In other words, the sulphuric acid had acted as an efficient oxidising agent. In another experiment, the acid was boiled with dilute sulphuric acid for two hours, but, in this case, the acid was recovered unchanged.

That the substance produced by heating  $\alpha$ -hydroxy- $\alpha$ -octyl-

acid is unsaturated is confirmed by the facts that it readily reduces potassium permanganate in alkaline solution in the cold, and under the influence of platinum black, absorbs hydrogen to give the saturated dicarboxylic acid,  $C_7H_{10}O_4$ , described on p. 2812. Its constitution was determined by investigating the products obtained when it is oxidised by potassium permanganate, as described below. Two quantities of 11 grams each of the acid were dissolved in a mixture of 170 c.c. of acetone and 20 c.c. of water, and to this, finely powdered potassium permanganate was added. Reduction took place immediately in the cold, and became more energetic on warming. Small quantities of permanganate were added from time to time to the boiling solution until there was no farther reduction. The acetone was then distilled off, the manganese dioxide dissolved by means of dilute sulphuric acid and sulphur dioxide, and the whole distilled in a current of steam (filtrate X). The mother liquor in the flask deposited, on cooling, a solid (9 grams), which was collected and dissolved in 250 c.c. of boiling water. This solution deposited, on cooling, a solid (1 gram), which was removed by filtration (filtrate Y), and then dissolved in hot water. The solution was neutralised with excess of magnesium carbonate and filtered while hot. The filtrate was concentrated to a syrup, allowed to cool, and the magnesium salt which separated was collected. It was again crystallised from water, and finally decomposed by heating with dilute hydrochloric acid. The acid thus obtained was crystallised from water, from which it separated in large, thin, glistening plates, melting at 106°. A mixture of equal parts of this acid and azelaic acid (m. p. 106°) melted at 106° (Found: M.W. 187.8;  $H_2O_4$  requires M.W. 188.)

Filtrate Y was evaporated to dryness, and the dried residue, melting at 90–126°, was extracted four times with ether, using 10 c.c. for each extraction. The undissolved residue melted at 138–140°, and, after crystallisation from water, melted at 138.5°. Found: C 55.02; H 8.20. M.W. 174.6.  $C_7H_{10}O_4$  requires C 54.1; H 8.10 per cent. M.W. 174.1.)

The substance was thus proved to be suberic acid.

Filtrate X was extracted with much ether, the ethereal solution washed once with water, dried, and evaporated, and the residue fractionally distilled. The fraction boiling at 234–242° was identified by analysis as *n*-octoic acid (b. p. 236–237°). Found: M.W. 142; Ag = 43.35.  $C_8H_{16}O_4$  requires M.W. 144. (For silver salt Ag = 42.98 per cent.)

The fraction boiling at above 245° (Found: M.W. 158;  $H_2O_4$  requires M.W. = 158) was converted, through the

sodium salt, into the zinc salt, which was shown to be an *n*-nonoate. The amount of substance dealt with did not allow of a complete separation and isolation in a pure state of the *n*-nonoic and *n*-nonoic acids, but the analysis showed that these acids were undoubtedly present in the mixture.

*Preparation of  $\alpha$ -Octylsebacic Acid,  $\text{CO}_2\text{H}\cdot\text{CH}(\text{C}_8\text{H}_{17})\cdot(\text{CH}_2)_7\cdot\text{CO}_2\text{H}$ , by Reduction of the Unsaturated Acids,  $\text{C}_{18}\text{H}_{34}\text{O}_4$ .*

This reduction was effected by the direct addition of hydrogen in the presence of spongy platinum. The catalyst was prepared by the reduction of platinum chloride by means of formic acid in the presence of sodium hydroxide (Loew, *Ber.*, 1896, 23; Willstätter, *Ber.*, 1912, 45, 1472; Hess, *Ber.*, 1913, 46, 1000) and was washed first with water and then with glacial acetic acid. Five grams of the unsaturated acids  $\text{C}_{18}\text{H}_{34}\text{O}_4$ , dissolved in 10 c.c. of glacial acetic acid, were reduced. The absorption of hydrogen was never very rapid, the quickest rate being about 50 c.c. in twenty minutes. Sometimes the hydrogen was under a pressure of about 20 cm. of mercury above the atmospheric pressure, but this did not appear to increase the rate of absorption. When no further reduction took place, the acetic acid solution was warmed, filtered, and the filtrate poured into water. The precipitated acid was collected and crystallised from a mixture of chloroform and light petroleum until its melting point was constant. The yield was 70 per cent. of the theoretical:

0.1350 gave 0.3405  $\text{CO}_2$  and 0.1350  $\text{H}_2\text{O}$ .  $\text{C}=68.79$ ;  $\text{H}=10.90$ .

0.2054 required 13.2 c.c. 0.1*N*- $\text{NaOH}$ . M.W.=311.2.

$\text{C}_{18}\text{H}_{34}\text{O}_4$  requires  $\text{C}=68.75$ ;  $\text{H}=10.90$  per cent. M.W.=310.

$\alpha$ -Octylsebacic acid,  $\text{CO}_2\text{H}\cdot\text{CH}(\text{C}_8\text{H}_{17})\cdot(\text{CH}_2)_7\cdot\text{CO}_2\text{H}$ , crystallises from a mixture of chloroform and light petroleum in aggregates of hard prisms, melting at  $71.5\text{--}72.5^\circ$ . It is readily soluble in alcohol, chloroform, or ether in the cold, sparingly soluble in benzene, and insoluble in light petroleum. It does not reduce an alkaline solution of potassium permanganate even when warmed, nor does it decolorise a solution of bromine in chloroform. A white silver salt was obtained on adding a solution of the silver salt of the acid to a solution of silver nitrate:

0.1540 gave 0.0622 Ag.  $\text{Ag}=40.39$ .

$\text{C}_{18}\text{H}_{32}\text{O}_4\text{Ag}_2$  requires  $\text{Ag}=40.86$  per cent.

Methyl  $\alpha$ -octylsebacate,  $\text{CO}_2\text{Me}\cdot\text{CH}(\text{C}_8\text{H}_{17})\cdot(\text{CH}_2)_7\cdot\text{CO}_2\text{Me}$ , was prepared by the interaction of the dry silver salt of the acid and methyl iodide in solution in dry benzene. It is an oily liquid

melting at  $230-233^{\circ}/25$  mm., and dissolves readily in the common organic solvents:

0.1580 gave 0.4054  $\text{CO}_2$  and 0.1636  $\text{H}_2\text{O}$ .  $\text{C} = 69.98$ ;  $\text{H} = 11.59$ .

0.1000 in 15.7840 benzene gave  $\Delta t = 0.307^{\circ}$ . M.W. = 322.

$\text{C}_{18}\text{H}_{20}\text{O}_2$  requires  $\text{C} = 70.11$ ;  $\text{H} = 11.19$  per cent. M.W. = 342.

The *amide*,  $\text{NH}_2\cdot\text{CO}\cdot\text{CH}(\text{C}_8\text{H}_{17})\cdot[\text{CH}_2]_7\cdot\text{CO}\cdot\text{NH}_2$ . One gram of the acid and 0.5 c.c. of thionyl chloride were warmed together in the water-bath for fifteen minutes, the product was dissolved in ether, and the ethereal solution poured into a concentrated, aqueous solution of ammonia. The precipitated amide was collected, washed with water, and crystallised from dilute alcohol, from which it separates in slender needles, melting at  $167-168^{\circ}$ , being soluble in water, ether, benzene, or chloroform in the cold, and dissolves readily in boiling alcohol:

0.1990 gave 15.6 c.c.  $\text{N}_2$  at  $20^{\circ}$  and 754 mm.  $\text{N} = 8.92$ .

$\text{C}_{18}\text{H}_{30}\text{O}_2\text{N}_2$  requires  $\text{N} = 8.97$  per cent.

#### *Synthesis of $\alpha$ -Hydroxy- $\alpha$ -octylsebacic Acid from $\theta$ -Ketomargaric Acid.*

Ten grams of pure, dry hydrogen cyanide and six drops of ethylamine were added to a solution of 10 grams of  $\theta$ -ketomargaric acid in 50 c.c. of dry chloroform. After remaining for fortnight in a well-stoppered bottle, kept in a cool place, the chloroform and excess of hydrogen cyanide were evaporated by means of a current of air, and the solid residue was dissolved in ether, the ethereal solution washed with dilute sulphuric acid, then with water, dried, and evaporated. The residue was hydrolysed by dissolving it in 80 c.c. of alcohol, previously saturated with dry hydrogen chloride. The mixture was left at the ordinary temperature for three and a-half days, and then boiled on the waterbath for eight hours. The resulting solution, on cooling, deposited 2½ grams of crystalline solid, melting at  $38-39^{\circ}$ , which was found to be the ethyl ester of the unchanged ketomargaric acid (see page 2807). This was removed by filtration, the filtrate separated to dryness, and the residue boiled for forty hours with 2½ grams of potassium hydroxide dissolved in a mixture of 50 c.c. of alcohol and 10 c.c. of water. The complete hydrolysis of the hydroxy-cyanide was difficult to effect, and, even after boiling for the period mentioned, traces of ammonia were still being evolved. The alcohol was evaporated, the residue diluted with water, and extracted with ether. The aqueous mother liquor was separated into dilute hydrochloric acid, the precipitated acid dissolved in ether, the ethereal solution washed, dried, and

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evaporated. The residue weighed 7.5 grams, and, after three crystallisations from chloroform, melted at 111–112°. A mixture of equal parts of this acid and  $\alpha$ -hydroxy- $\alpha$ -octylsebacic acid melted at exactly the same temperature:

0.1371 gave 0.3270  $\text{CO}_2$  and 0.1286  $\text{H}_2\text{O}$ .  $\text{C}=65.05$ ,  $\text{H}=10.38$ .

0.2254 required 13.5 c.c. 0.1N-NaOH.  $\text{M.W.}=333.9$ .

$\text{C}_{18}\text{H}_{34}\text{O}_2$  requires  $\text{C}=65.40$ ;  $\text{H}=10.38$  per cent.  $\text{M.W.}=334$ .

The synthetic acid, like the original  $\alpha$ -hydroxy- $\alpha$ -octylsebacic acid, readily loses water when heated, to give a liquid which readily reduces potassium permanganate. When oxidised with potassium permanganate in acetone solution, the synthetic acid gives a monobasic acid melting at 78–79°, identical with  $\theta$ -ketomargaric acid obtained by the oxidation of  $\alpha$ -hydroxy- $\alpha$ -octylsebacic acid. This identity was fully confirmed by the fact that a mixture of equal parts of the two acids melted at 74–75°. Further, the methyl ester of the ketonic acid obtained from the synthetic acid had all the properties of methyl  $\theta$ -ketomargaric

#### *Preparation of Dihydroxybehenic Acid.*

The method employed for the oxidation of erucic acid differs somewhat from that used by Hazura and Grüssner (*Mém. Chim. Phys.* 1888, 9, 948), and since these observers obtained a yield of only 25 per cent. of the theoretical, whereas ours amounted to 75 per cent., we give the essential details of the method we used. Ten grams of erucic acid (m. p. 33°) and 14 grams of potassium hydroxide were dissolved in 2 litres of water, the solution cooled to 0°, and maintained at this temperature during the whole of the oxidation. A solution of 32 grams of potassium permanganate in 1500 c.c. of water was then added drop by drop to the solution, which was kept well stirred by means of a turbine. When the mixture was allowed to remain over night, the manganese dioxide dissolved by means of dilute sulphuric acid and sulphur dioxide, and the precipitated acid filtered and crystallised from alcohol.

#### *Preparation of $\alpha$ -Hydroxy- $\alpha$ -nonyldodecanedicarboxylic Acid.* $\text{CO}_2\text{H}\cdot\text{C}(\text{OH})(\text{C}_9\text{H}_{19})[\text{CH}_2]_{11}\cdot\text{CO}_2\text{H}$

Twenty grams of dihydroxybehenic acid (m. p. 127–128°) and 20 grams of potassium hydroxide, and 40 c.c. of water were heated together in a nickel crucible, and the whole gradually heated in a metal-bath to 240–245°, and maintained at this temperature for one hour, the fused mass being stirred continuously. The mass was dissolved in water, acidified with dilute sulphuric acid, and the precipitated acid dissolved in ether. The ethereal solution

was washed, dried, evaporated, and the residue crystallised from chloroform and then from acetone until its melting point was constant. The yield was 64 per cent. of the theoretical:

0.1233 gave 0.3083  $\text{CO}_2$  and 0.1213  $\text{H}_2\text{O}$ . C = 68.19; H = 11.01.

0.178 required 11.3 c.c. 0.1N-NaOH. M.W. = 385.6.

$\text{C}_{20}\text{H}_{40}\text{O}_3$  requires C = 68.33; H = 10.96 per cent. M.W. = 386.34.

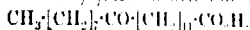
$\alpha$ -Hydroxy- $\alpha$ -octyldodecanedicarboxylic acid is sparingly soluble in alcohol, acetone, or benzene in the cold, but dissolves readily on heating; it is sparingly soluble in hot ether, and is insoluble in light petroleum. It crystallises from acetone in needles, melting at 115–116°. The white silver salt was obtained on adding a warm solution of the sodium salt of the acid to a warm solution of silver nitrate:

0.106 gave 0.0784 Ag. Ag = 35.54.

$\text{C}_{22}\text{H}_{40}\text{O}_5\text{Ag}_2$  requires Ag = 35.96 per cent.

When the acid is heated, it behaves exactly like  $\alpha$ -hydroxy- $\alpha$ -sthebaic acid, in that it readily loses the elements of water. The product is a viscid oil, which shows no signs of solidifying when kept for several weeks. It readily reduces an alkaline solution of potassium permanganate, but does not decolorise a solution of bromine in chloroform.

#### Preparation of $\mu$ -Ketohexicosonic Acid,



Eight grams of  $\alpha$ -hydroxy- $\alpha$ -octyldodecanedicarboxylic acid were dissolved in a mixture of 120 c.c. of acetone and 20 c.c. of water, and finely powdered potassium permanganate was added to the solution. There was no action in the cold, but, on warming, reaction immediately took place, and became very energetic at the boiling point of the acetone. The permanganate was added in small quantities at a time until no further oxidation took place. The acetone was evaporated, the manganese dioxide dissolved by means of dilute sulphuric acid and sulphur dioxide, and the precipitated acid collected and crystallised from acetone:

0.1194 gave 0.3240  $\text{CO}_2$  and 0.1273  $\text{H}_2\text{O}$ . C = 74.01; H = 11.93.

0.290 required 15.5 c.c. 0.1N-NaOH. M.W. = 339.4.

$\text{C}_{26}\text{H}_{50}\text{O}_3$  requires C = 74.05; H = 11.85 per cent. M.W. = 340.32.

$\mu$ -Ketohexicosonic acid is readily soluble in cold chloroform, sparingly so in alcohol, benzene, or ether, and insoluble in light petroleum. It crystallises from acetone in glistening, micaceous plates, melting at 89–90°. The white silver salt was obtained by adding a warm solution of the sodium salt to a warm solution of silver nitrate:

0.2224 gave 0.0538 Ag. Ag = 24.19.

$C_{21}H_{32}O_3$  Ag requires Ag = 24.16 per cent.

*Methyl  $\mu$ -ketoheneicosate*,  $CH_3[CH_2]_{11}CO[CH_2]_{11}COOMe$ , prepared by the method used for the preparation of methyl  $\theta$ -ketomargarate (p. 2806), and was purified by crystallization from methyl alcohol, from which it separates in glistening leaflets, melting at 59–60°. It is readily soluble in ether, cold benzene in the cold, and dissolves sparingly in cold methyl alcohol:

0.1296 gave 0.3535  $CO_2$  and 0.1402  $H_2O$ . C = 74.39; H = 11.95.

$C_{22}H_{42}O_3$  requires C = 74.50; H = 11.95 per cent.

*Ethyl  $\mu$ -ketoheneicosate*,  $CH_3[CH_2]_{11}CO[CH_2]_{11}COEt$ , prepared by the method used for the preparation of the methyl ester, and was crystallized from dilute alcohol, from which it separates in glistening leaflets, melting at 56°. It is sparingly soluble in cold alcohol, and dissolves readily in the other common organic solvents:

0.1463 gave 0.4010  $CO_2$  and 0.1593  $H_2O$ . C = 74.75; H = 12.04.

$C_{23}H_{44}O_3$  requires C = 74.90; H = 12.04 per cent.

The *semicarbazone* was prepared by the method employed in the preparation of the semicarbazone of  $\theta$ -ketomargaric acid, and was purified by crystallization from acetone, from which it separates in aggregates of slender needles, melting at 104–105°. It is sparingly soluble in boiling acetone or ethyl acetate, and is soluble in light petroleum or ether:

0.1978 gave 18.6 c.c.  $N_2$  at 22° and 763 mm. N = 10.71.

$C_{22}H_{43}O_3N_3$  requires N = 10.58 per cent.

#### *Synthesis of $\alpha$ -Hydroxy- $\alpha$ -octyldodecanedicarboxylic Acid from $\mu$ -Ketoheneicosic Acid.*

The method used to effect this synthesis was practically identical with that employed for the preparation of  $\alpha$ -hydroxy- $\alpha$ -octylundecanedicarboxylic acid from  $\theta$ -ketomargaric acid. The addition of the hydroxy cyanide in this case also was very slow, and the complete hydrolysis of the hydroxy cyanide difficult to effect. The crude acid was crystallized from chloroform until its melting point was constant, at 115–116°. A mixture of equal parts of this acid and the original  $\alpha$ -hydroxy- $\alpha$ -octyldodecanedicarboxylic acid melted at exactly the same temperature:

0.1115 gave 0.2788  $CO_2$  and 0.1094  $H_2O$ . C = 68.20; H = 10.96.

0.2590 required 13.0 c.c. 0.1N-NaOH. M.W. = 398.

$C_{22}H_{42}O_6$  requires C = 68.33; H = 10.96 per cent. M.W. = 398.

In order to confirm further the identity of the synthetic

the  $\alpha$ -hydroxy- $\alpha$ -octyldodecanedicarboxylic acid obtained by the fusion of dihydroxybehenic acid with potassium hydroxide, a small quantity of it was oxidised with potassium permanganate in aqueous solution, when an acid was obtained which melted at 136°, and had all the properties of the  $\alpha$ -ketoheneicosoic acid produced by the oxidation, under similar conditions, of  $\alpha$ -hydroxy- $\alpha$ -tridecanedicarboxylic acid.

*Constitution of the Ketonic Acid,  $C_{21}H_{40}O_5$ .*

The oxime of the acid,  $C_{21}H_{40}O_5$ , was prepared by the method described on page 2807, and was converted into the corresponding amine by heating with five times its volume of concentrated ammonia acid for two and a-half hours on the water bath. The product was poured on crushed ice, and the solid collected and recrystallised from glacial acetic acid containing a little water, from which it separates in aggregates of stout prisms, melting at 174–176°.

Found, N: 4.02.  $C_{21}H_{40}O_5N$  requires N: 3.91 per cent.

The above isomeric amides were hydrolysed by heating with dilute hydrochloric acid in a sealed tube, as described on page 2808. The product was diluted largely with water, and distilled in a current of steam (distillate 1). The residue was then made strongly alkaline and distilled in a current of steam (distillate 2).

Distillate 1 was extracted with ether, the ethereal solution washed, dried, evaporated, and the residue distilled, when it all passed over at 150–155°, 31 mm. It was fractionally distilled under the ordinary pressure, and the fraction boiling at 218–219° was collected for analysis. It readily solidified when cooled in ice. Found, M.W. = 157.9.  $C_{17}H_{34}O_2$  requires M.W. = 158.1. The potassium salt was prepared in the usual way, and, after crystallisation from alcohol, melted at 136°, proving the acid to be  $\alpha$ -nonoic acid.

Distillate 2.—The amine was isolated from this distillate as described on page 2809, and was obtained as a clear, colourless liquid, boiling at 174–176°, which was identified as octylamine by analysis of the platinumchloride (Found, Pt 29.07. Calc., 29.21 per cent.), and by the preparation of phenyloctylphosphate which melted at 79–80°.

The mother liquor left after obtaining distillate 2 was concentrated to about 350 c.c., and then poured into a slight excess of concentrated hydrochloric acid. The solid which separated on cooling was collected, dried, and boiled with 50 c.c. of alcohol. The solution was filtered, and the filtrate concentrated to about



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20 c.c., and then mixed with 50 c.c. of ether, when a voluminous crystalline mass separated. This was collected (filtrate 3.14), crystallised from hot water, from which it separates in thin lamellæ, melting at 163°:

0.1782 gave 8.8 c.c.  $N_2$  at 20° and 778 mm.  $N=5.75$

$C_{12}H_{23}O_2N.HCl$  requires  $N=5.57$  per cent.

A portion was converted into the *platinichloride*, which *decomposes* at 209°:

0.2394 gave 0.0550 Pt.  $Pt=22.97$ .

$(C_{12}H_{23}O_2N)_2.H_2PtCl_6$  requires  $Pt=23.21$  per cent.

The substance is therefore the *hydrochloride* of *aminolauric acid*,  $CO_2H.(CH_2)_{11}.NH_2.HCl$ . It is insoluble in hot or cold water, benzene, chloroform, or acetone, freely soluble in alcohol, and moderately so in water.

The free amino-acid was isolated by adding the calculated volume of a dilute sodium hydroxide solution to a warm, aqueous solution of the above pure hydrochloride. The white, crystalline mass which separated was collected, washed with cold water, and dissolved in boiling water, from which it crystallised on cooling in long, thin plates with almost square ends:

0.0942 gave 0.2306  $CO_2$  and 0.0982  $H_2O$ .  $C=66.76$ ;  $H=11.71$

0.1574 „ 9.0 c.c.  $N_2$  at 18° and 770 mm.  $N=6.70$ .

$C_{12}H_{23}O_2N$  requires  $C=66.91$ ;  $H=11.71$ ;  $N=6.51$  per cent.  
 $\alpha$ -Aminolauric acid,  $NH_2.(CH_2)_{11}.CO_2H$ , melts at 144°, and is practically insoluble in the common organic solvents.

In order more completely to characterise the acid, its  $\beta$ -naphthalenesulphonyl derivative was prepared. For this purpose a mixture of the amino-acid (1 mol.), *N*-sodium hydroxide (1.5 mols.) and an ethereal solution of  $\beta$ -naphthalenesulphonyl chloride (2 mols.) was shaken in a stoppered bottle. At intervals of 1 hour, three more molecular proportions of sodium hydroxide were added, and the shaking was prolonged altogether for five hours. The mass was diluted with water and allowed to flow into dilute sulphuric acid, the ethereal layer being retained in a separating funnel. The white solid which separated was collected, washed free from sulphuric acid, and dissolved in hot 25 per cent. alcohol, from which it crystallised in small flakes, melting at 157°:

0.1238 gave 3.8 c.c.  $N_2$  at 18° and 750 mm.  $N=3.50$ .

$C_{22}H_{31}O_4NS$  requires  $N=3.46$  per cent.

$\alpha$ - $\beta$ -Naphthalenesulphonylaminolauric acid,

$C_{30}H_{37}.SO_2.NH.(CH_2)_{11}.CO_2H$ ,

is readily soluble in hot alcohol, sparingly so in cold alcohol, ether, acetone, or water, and insoluble in light petroleum.

The alcohol-ether filtrate 3 (p. 2818) was evaporated on the water-bath, and the residue diluted with water. On leaving this solution, crystals soon separated; these were collected, and crystallised first from water and then from benzene, from which the substance was deposited as a crystalline powder, melting at  $113.5^{\circ}$ . (Found: C = 63.89; H = 9.92. M.W. = 247.2.  $C_{15}H_{24}O_4$  requires C = 63.88; H = 9.91 per cent. M.W. = 244.19.) A portion was converted into the silver salt (Found: Ag = 46.89.  $C_{15}H_{22}O_4Ag_2$  requires Ag = 47.11 per cent.) and another portion into the amide, which melted at  $174-175^{\circ}$ . (Found: N = 11.66.  $C_{15}H_{26}O_2N_2$  requires N = 11.57 per cent.)

The dicarboxylic acid which resulted from the hydrolysis of the above mixture of isomeric amides was thus fully identified with brassylic acid,  $CO_2H[CH_2]_{11}CO_2H$ . Fileti and Pouzio (*J. pr. Chem.*, 1893, [ii], **48**, 323) found as the melting point of brassylic acid  $114^{\circ}$ , and of the amide  $177^{\circ}$ .

The yields of the four substances obtained by the hydrolysis of the above mixed amides were as follows:

Nonanoic acid .....	90 per cent. of the theoretical.
undecylamine .....	89   "   "   "
Brassylic acid .....	57   "   "   "
Hydrochloride of $\alpha$ -aminolauric acid.....	55   "   "   "

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#### CLXIV.—*The Polysulphides of the Alkali Metals.* *Part II. The Polysulphides of Potassium.*

By ALEXANDER RULE and JOHN SMEATH THOMAS.

In a previous paper (Rule and Thomas, this vol., p. 177) were described the results of an investigation of the action of sulphur on alcoholic solutions of pure sodium hydrosulphide. It was shown that the reaction provided a simple and certain means of preparing sodium tetrasulphide in the pure anhydrous state, and further, that the polysulphide product obtained as a result of the reaction under stated conditions consisted almost entirely of the tetrasulphide.

It has been pointed out by several authors that much of the earlier work on the polysulphides of sodium and potassium is quite trustworthy, but descriptions of series of these compounds based on the results of such work still appear in many text-books. In the case of potassium the highest polysulphide obtainable is generally

accepted to be the pentasulphide, which seems to be fairly well characterised.

Bloxam (*Thesis*, London, 1898; *T.*, 1900, **77**, 753), in continuing the work of previous authors, has shown that by the method usually adopted it is impossible to obtain pure polysulphides in the solid state. When aqueous solutions of the monosulphide are employed the resulting product always contains thiosulphate. Bloxam attributed the formation of that compound to the presence of hydroxides in the solution as a result of the hydrolysis of the monosulphides.

Bloxam investigated the action of sulphur on aqueous solutions of potassium hydrosulphide, which is only very slightly hydrolysed (compare Walker, *Zeitsch. physikal. Chem.*, 1900, **32**, 155). Although he does not appear to have succeeded in isolating any compound of undoubted chemical individuality, yet he established the fact that within certain limits the sulphur added to the solution reacted with a portion only of the hydrosulphide, and the resulting polysulphide product was richer in sulphur than a polysulphide corresponding to the amount of sulphur added. It is probable that in aqueous solution there is a tendency for the formation of the predominating polysulphide, and this would account for Bloxam's results, as that author has pointed out. In the case of anhydrous solutions the work described in the present paper proves that the action of sulphur tends undoubtedly to the formation of one polysulphide only, namely, the pentasulphide, which has been isolated in the pure anhydrous condition.

The preparation of anhydrous potassium pentasulphide by the action of sulphur on potassium in liquid ammonia has also been described by Hugot (*Compt. rend.*, 1899, **129**, 388), but no account is given of the properties of the product.

#### *Action of Sulphur on Alcoholic Solutions of Potassium Hydrosulphide.*

In a previous paper (*T.*, 1911, **99**, 558) one of us described the preparation of pure potassium hydrosulphide by the action of hydrogen sulphide on an alcoholic solution of potassium ethoxide. In the work now under consideration solutions prepared in that way were used throughout, and the actual experimental details were precisely similar to those already described in the paper on the polysulphides of sodium (*loc. cit.*), to which reference may be made.

A series of experiments was carried out in which quantities of sulphur corresponding with possible polysulphides of potassium from the di- up to the hexa-sulphide were added to alcoholic

ness of the hydrosulphide of the same concentration throughout, and the only polysulphide product obtained as a result of these experiments was the pentasulphide the preparation and properties of that compound will be dealt with in the first place.

#### *Potassium Pentasulphide.*

One gram of potassium was dissolved in 15 c.c. of absolute ethyl alcohol, and the solution was saturated with dry hydrogen sulphide. 1.64 Grams of finely ground recrystallised rhombic sulphur were added, and the solution was boiled gently on a water-bath for about one hour, a rapid current of dry hydrogen being passed through it. On the addition of the sulphur a vigorous action at once took place even in the cold with evolution of hydrogen sulphide, and the solution became deep red. The sulphur subsided, and after a short time a bright orange-red, crystalline product separated out. The solution was concentrated to about 5 c.c., the product collected on a filter, sprayed with alcohol, and kept in a vacuum over phosphoric oxide.

The dry product consisted of a mass of glistening crystals, and appeared to be perfectly homogeneous. The yield was 2.5 grams, or 82 per cent. of the theoretical amount:

0.3500 gave 0.2560  $K_2SO_4$ .  $K = 32.73$ .

0.3475 .. 0.1850 S.  $\dagger(S) = 53.23$ .

0.3027 .. 1.4742  $BaSO_4$ .  $S = 66.90$ .

$K_2S_5$  requires  $K = 32.77$ ;  $(S) = 53.78$ ;  $S = 67.22$  per cent.

Potassium pentasulphide is extremely hygroscopic, and is rapidly oxidised on exposure to the air, with liberation of sulphur. It swells readily in water to form a clear, deep orange solution, which becomes dark red on heating. It is only sparingly soluble in alcohol, forming a red solution, which also becomes darker on heating. Both the aqueous and alcoholic solutions soon begin to deposit sulphur when allowed to remain in the air. Biltz and Fehrt (*Ber.*, 1905, **43**, 53) state that rubidium pentasulphide is easily decomposed on treatment with water, whilst caesium pentasulphide is apparently not affected. It is noteworthy that potassium pentasulphide should be more stable in this respect than the corresponding rubidium compound.

On heating in a capillary tube the substance begins to darken at about  $130^\circ$ , and at  $182^\circ$  becomes quite black, this change being easily marked; it begins to sinter at  $200-205^\circ$ , and melts not very sharply at about  $220^\circ$ . On cooling the substance passes through

\* Commercial absolute alcohol was shaken for two days over freshly prepared calcium, boiled over quicklime and then distilled.

<sup>†</sup> S. is about a "polysulphide sulphur."

the same series of colour changes in the reverse order, and the solid assumes its original appearance. No deposit of sulphur was observed on the walls of the tube, and the solidified product dissolved in a perfectly clear solution in cold water. Potassium pentasulphide can therefore be fused without decomposition.

The majority of organic solvents are without action on the pentasulphide, but a very striking behaviour may be noted in the case of pyridine. On treating the substance with pure pyridine the latter is coloured an intense brownish-red, and on heating the mixture the liquid becomes quite opaque. A definite reaction appears to take place, and the observed effect may be due to the formation of an additive compound, but apparently very unstable. The pentasulphide dissolves in the pyridine. With sodium tetrasulphide the action of pyridine is even more marked, the liquid being at once coloured intensely green and the solid slowly changing in colour to bright yellow. This action is being further investigated.

Nitrobenzene, on treatment with the pentasulphide, is coloured magenta in the cold. On heating the colour fades, and the solid can be fused below the liquid; on cooling again the colour returns, and the pentasulphide remains apparently unchanged. This behaviour with nitrobenzene is similar to that of rubidium polysulphide, as noted by Biltz and Dörfurt (*loc. cit.*).

When shaken with alcohol at the ordinary temperature the pentasulphide forms a well-defined, bright yellow alcoholate, which crystallises in small, monoclinic prisms.

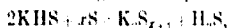
From a consideration of the results obtained by numerous workers in this field it appears to have been generally assumed that a series of polysulphides from the di- up to the pentasulphide can be prepared by adding the theoretical amount of sulphur to aqueous solutions of the mono- or hydro-sulphide. The results obtained from the use of alcoholic solutions of sodium hydrosulphide and varying quantities of sulphur have already been dealt with in detail (*loc. cit.*), and it is therefore only necessary to mention briefly the nature of the products of the action of sulphur on alcoholic solutions of potassium hydrosulphide. With the proportions for the disulphide a small quantity of pentasulphide separated from the hot solution, and on cooling a yellow product was obtained, which was obviously not homogeneous, and consisted of a mixture of pentasulphide and unchanged hydrosulphide. A similar result was obtained when proportions for the trisulphide were used, but the yield of pentasulphide was greater.

With the proportions for the tetrasulphide a comparatively con-

of pure pentasulphide was obtained, separating out from the solution. With the proportions for a possible hexasulphide it was found that all the sulphur added dissolved in the first place, and the solid product consisted of the pentasulphide mixed with a little sulphur, which remained undissolved on treating the product with water. The solution from which this product separated gave no precipitate of sulphur on treatment with water, whereas in all other cases mentioned the solution remained perfectly clear.

The results are therefore very similar to those obtained in the case of sodium, except that here there is not the slightest indication of the formation of higher polysulphides when larger quantities of sulphur than that corresponding with the pentasulphide are used. The moderate solubility of potassium pentasulphide in alcohol has already been mentioned, and it might therefore be assumed that this compound is the saturation product, and that in the solution a series of polysulphides might exist in equilibrium according to the conditions of experiment. In order to test the accuracy of this assumption and to gain some idea as to the nature of the substances in solution after the action of sulphur on the hydrosulphide, a series of measurements similar to those described in connection with the polysulphides of sodium was carried out.

It will be seen that according to the equation:



the amount of hydrogen sulphide formed is strictly proportional to the amount of hydrosulphide involved in the reaction. By determining the amounts of hydrogen sulphide evolved in the course of a series of reactions with different amounts of sulphur it is possible to decide whether (1) a series of polysulphides is formed according to the amount of sulphur added, (2) only one polysulphide is formed independent of the amount of sulphur present, or whether (3) an equilibrium mixture of several polysulphides is formed.

The apparatus used and the method adopted were exactly similar to those employed in the case of sodium (*loc. cit.*), except that sodium hydroxide was used throughout as the reagent for hydrogen sulphide instead of bromine. Owing to the moderate solubility of potassium pentasulphide in alcohol, and the necessity of preventing any solid product from separating out during the experiment, it was necessary to work with fairly dilute solutions of the hydrosulphide, and an error is thereby introduced owing to the fact that the hydrosulphide undergoes slight alcoholysis with the formation of hydrogen sulphide. Since it was necessary to carry out the determination in a stream of hydrogen the equilibrium was constantly disturbed, and in consequence a

certain amount of hydrogen sulphide derived from this solution was driven over into the absorbent. In consequence the values obtained are too high. For the purpose of ascertaining the magnitude of this error, blank experiments, in which the solution approximated as nearly as possible to those employed in the actual determinations, were performed first of all with solutions of potassium hydrosulphide of varying concentration. Using a 0.5N solution it was found that after boiling in a current of hydrogen for forty five minutes the amount of hydrogen sulphide evolved calculated for 72 grams of potassium hydrosulphide was 0.31 gram. A 0.5N solution under similar conditions gave 1.2 grams.

It will be seen that the amount of unchanged hydrosulphide remaining in solution decreases progressively with addition of sulphur, and therefore the error decreases as the amount of sulphur increases. In order to overcome this error as far as possible the concentration of the hydrosulphide solutions used was varied from 0.5N to 0.25N, the effect of this being to keep the solutions saturated with respect to the pentasulphide formed, assuming this to be the chief product of the reaction, throughout the series of determinations.

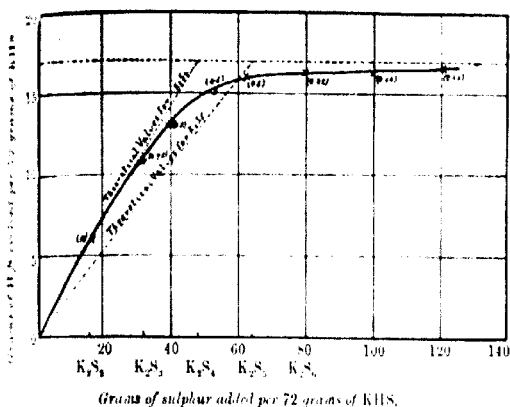
The results are expressed graphically in the diagram; the values in brackets at the various points on the curve indicate the concentrations of the hydrosulphide solutions in terms of normality.

The results show that there is a gradual increase in the amount of hydrogen sulphide evolved with increase in the amount of sulphur added. In the diagram the theoretical straight lines are shown which would indicate the values for the tetrasulphide and pentasulphide if these were the only polysulphides respectively formed in the course of the reaction.

The curve at first approximates very closely to the values for tetrasulphide, but then bends away and eventually crosses the pentasulphide line not far away from the maximum, after which the values become practically constant. Taking into consideration the effect of alcoholysis it may be stated that all the values on the left-hand branch of the curve lie below the tetrasulphide line. Although the lower values possibly indicate the presence of polysulphides lower than the pentasulphide in the solution, and not especially of the tetrasulphide, it must be noted that unchanged hydrosulphide still remains in solution below the pentasulphide stage, and it is not until the amount of sulphur corresponding to the pentasulphide is present that the amount of hydrogen sulphide evolved is approximately equal to the maximum obtained in the series of determinations.

It is clear that when quantities of sulphur less than those corre-

leading with the tetrasulphide are used, very little di- or tri-sulphide, if any, can be formed, otherwise the values for hydrogen sulphide at these stages would be much higher. On the other hand, since the value at the pentasulphide stage is very near the theoretical maximum for hydrogen sulphide there is no indication of the presence of any higher polysulphides in solution (compare the curve for sodium hydrosulphide, *loc. cit.*). As a result of this investigation, therefore, as well as from the results of experiments in which the solid was allowed to separate out, it is fair to conclude that the chief product of the action of sulphur on potassium hydrosulphide under the conditions described is the pentasulphide, and at the same time it is obvious that it is impossible to obtain



the lower polysulphides simply by adding the equivalent quantity of sulphur to solutions of the hydrosulphide.

#### *Solubility of Sulphur in Alcoholic Solutions of Potassium Hydrosulphide.*

It has already been shown by Küster and Heberlein (*Zeitsch. anorg. Chem.*, 1905, **43**, 53) that aqueous solutions of sodium monosulphide are able to dissolve considerably more sulphur than is represented by any polysulphide hitherto isolated. The present authors have also shown (*loc. cit.*) that alcoholic solutions of sodium polysulphide under certain conditions dissolve sulphur to an extent represented by the formula  $\text{Na}_2\text{S}_{6.9}$ . A similar determination was made in the case of potassium hydrosulphide. It has been pointed out above that the solution is capable of dissolving at least



a proportion of sulphur corresponding with a possible hexasulphide, although such a product does not separate out.

A 0.25*N* solution of the hydrosulphide was shaken with excess sulphur in a flask in a thermostat at 25° for forty-eight hours, a continuous current of dry hydrogen being passed through the solution. The solution was then allowed to settle, and a portion removed by means of a pipette, introduced into bromine water, made up to 1 litre, and the potassium and sulphur determined in aliquot portions:

250 c.c. gave 0.1247  $K_2SO_4$ ,  $K = 0.0559$ .

250 „ „ 1.0774  $NaSO_4$ ,  $S = 0.148$ .

Atomic ratio,  $K : S = 3.23$ , corresponding with  $K_3S_{10}$ .

In the case of sodium hydrosulphide, using a 2*N* solution at 25° the ratio found was 2 : 6.36, and at 81° it was 2 : 6.2, but a figure for the higher temperature is rather difficult to determine with accuracy.

The addition of water to these solutions resulted in a complete precipitation of sulphur, and the same holds good for all solutions containing sulphur in proportions higher than that corresponding with the pentasulphide. It must be noted that in these experiments the solubility of sulphur in alcohol is not taken into account, in any case it is so small as to have very little effect on the result.

#### *Action of Metallic Potassium on Alcoholic Solutions of the Pentasulphide.*

When alcoholic solutions of sodium tetrasulphide are treated with metallic sodium, reduction of the polysulphide takes place, and practically pure sodium disulphide separates out. A series of experiments was performed in order to determine if metallic potassium had a similar action on the pentasulphide. Reduction certainly takes place, but in no case were the products obtained monomeric compounds, but rather mixtures of lower polysulphides with unchanged pentasulphide. When excess of potassium was used the solution became paler in colour, and a yellow product separated out, which on analysis approximated to the trisulphide, but the figure for polysulphide sulphur was too high.

In other experiments with more dilute solutions and smaller amounts of potassium the products always contained unchanged pentasulphide, which appears to be "salted out" from the solution by the potassium ethoxide formed. In all cases the figure for polysulphide sulphur was higher than that required for the trisulphide. The method therefore does not provide a means of arriving at a definite lower polysulphide as in the case of sodium, and conse-

the sensitive nature of the products separation of the component compounds would be a difficult operation.

### General Conclusions.

Although it cannot be claimed that the results of this investigation throw any further light on the actual constitution of the polysulphides, yet it may afford some evidence as to the extent to which sulphur can be taken up by any one member of the series of alkali metals to form a stable polysulphide. Biltz and Dorfürst (*Zeitsch. anorg. Chem.*, 1906, **48**, 297; **50**, 67) were successful in obtaining both the tetra- and penta-sulphides of rubidium and caesium by the action of sulphur on aqueous solutions of the monosulphides. These compounds are perfectly well defined, and moreover, the authors mentioned were able to show the existence of hexasulphides which were characterised thermo-analytically in the course of a freezing-point curve determination. It is hoped yet to give the results of a similar determination for potassium sulphur and sodium sulphur, but in the meantime it may be noted that no evidence has been obtained in the course of the authors' experiments of the existence of potassium hexasulphide.

Taking into consideration the results of the work on potassium, rubidium, and caesium, we are able to recognise three definite and stable pentasulphides exhibiting a gradation in respect of certain properties, for example, solubility. The solubility in alcohol increases with increase in atomic weight of the alkali metal, and it is fair to assume that the solubility in water would vary in the same direction, thus bringing these compounds into line with other series of salts of the same metals, such as the alums, platinum-bromides, etc.

In the case of sodium we find that the highest stable polysulphide is the tetrasulphide, and although under certain conditions there is a tendency to form higher polysulphides, yet there is no definite trace of the existence of a pentasulphide in the solid state, though the  $S_5^{2-}$  anion may be present in solution.

Practically nothing is known concerning polysulphides of lithium, though a disulphide is supposed to exist.

It would be interesting to determine if, by working with alcoholic solutions of rubidium and caesium hydrosulphides, the hexasulphides of these metals would separate out as stable compounds in the solid state, and the authors hope to carry out this investigation very shortly.

The fact that alcoholic solutions of sodium tetrasulphide and caesium pentasulphides are still able up to a certain point to take further quantities of sulphur demonstrates the tendency of

the sulphur complex in each case to combine with more sulphur. At the same time, however, this additional sulphur is precipitated in a looser state of combination than that in the stable complex itself, since it is precipitated on the addition of water to the solution. It is possible that the tetrasulphide complex in the case of sodium, and the pentasulphide complex in the case of potassium represent the limits within which ordinary valency considerations apply, and that the sulphur which dissolves over and above these stages may be loosely associated to the complex as a result of the residual affinity exerted by the latter.

These facts taken in conjunction with the work on rubidium and caesium point to the distinct influence of the metal itself on the number of atoms in the stable sulphur complex, and this view is also taken by Biltz and Dörfurt, who apply the well-known valency affinity theory of Abegg and Bodländer (*Zeitsch. anorg. Chem.*, 1899, 20, 457) to account for the formation of higher polysulphides of the alkali metals of higher atomic weight.

Abegg and Bodländer show that where the ionising tendency (Ionisierungstendenz) of the metal is considerable that tendency is imparted to the anion which may normally show a weak ionising tendency. The anion, in order to "strengthen" itself, tends to combine with other atoms or groups to form a complex. The ionising tendency of the alkali metals is shown to increase with increase of atomic weight, and Biltz and Dörfurt apparently consider that, in the case of the polysulphides, as the atomic weight of the metal increases there will be an increase in the number of sulphur atoms which go to make up the highest stable complex.

On the other hand, Hamburger and Abegg (*Zeitsch. anorg. Chem.*, 1906, 50, 437) in discussing the results of an investigation of the polyiodides of the alkali metals consider that in solutions of different degrees of complexity are present, and that the particular polyiodide which separates out depends entirely on the particular ionic combination the solubility product of which is exceeded. Moreover, it does not follow that the compound which separates out will represent a combination of the cation with the anion present in greatest concentration. The fact that the polyiodides are more readily formed as we pass up the series of alkali metals from lithium to caesium is explained on the basis that the solubilities of the higher polyiodides decrease in this order, like the platinumchlorides, etc.

Abegg and Bodländer have shown that this inverse-solubility is frequently exhibited in the case of strong anion combinations with increasingly strong cations, and a normally weak anion becomes stronger owing to addition resulting in the formation

complexes, a fact which is in agreement with the electro-affinity of sulphur. It will be seen that Hamburger and Abegg (*loc. cit.*), in dealing with the polyiodides, and in referring also to the work of Biltz and Berfart, do not consider that the cation has a definite influence on the particular number of atoms taken up by the anion to form a complex, but only on the formation of complexes in general, the degree of the substance separating out depending on local conditions.

So far as the polysulphides are concerned, the work of the most authors does undoubtedly show the tendency for the formation of one particular polysulphide ion in greatly predominating amount, in the case of sodium the tetrasulphide ion, and in that of potassium the pentasulphide ion. At present, however, further speculations must be withheld until data are collected sufficient to test these conclusions.

The authors are indebted to Mr. F. Fowweather, B.Sc., for assistance in carrying out a portion of the experimental work.

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## CXLV.—*The Removal of Sulphur from Silver.*

By CRELLYN COLGRAVE BISSETT.

It is well known that sulphur is found at times in silver, especially in the metal recovered from materials containing thiocyanates, has been mentioned by the author in a previous paper (this vol., p. 271). When recovering metal from such residues the danger can be removed to a large extent by a preliminary digestion of the metal with warm concentrated hydrochloric acid. The last traces of sulphur can be removed by the addition of a little potassium carbonate to the sodium carbonate used in the recovery.

The removal of sulphur from metallic silver by fusion with sodium nitrate is very tedious, as the oxidation proceeds very slowly. It appeared possible that the sulphur could be removed more readily by the addition of the necessary quantity of a second metal. The results obtained by adding copper and iron respectively have been studied to some extent. The effect produced by passing air through the molten metal has also been determined.

The results obtained by the metallic additions have a great interest, since they show the nature of the chemical reaction in these cases at moderately high temperatures.

### I. Influence of Copper on Silver containing Sulphur

The freezing point diagram for the mixture silver-cuprous sulphide has been determined by Friedrich (Mett., 1907, 4, 671), who found that mixtures of these substances form an unbroken series of solid solutions, the freezing-point curve reaching a minimum at 70 per cent. of silver sulphide, the freezing-point of this mixture being  $677^{\circ}$ .

Cuprous sulphide is the only sulphide of copper stable at high temperatures.

The results given below tend to show that the reaction between the sulphides is not affected by the presence of any of either or both of the metals.

The effect produced by adding copper to silver containing 10 per cent. of silver sulphide was first studied. It was found that the addition of small amounts of copper caused the first freezing point of the alloy to be lowered, whilst at the same time the temperature of the halt in the cooling curve due to the materials being completely miscible in the liquid state was raised. This change continued until 2 per cent. of copper had been added; the mixture then had only one main freezing point. An examination of a vertical section of the ingot at this stage showed that the materials had separated into two layers in the liquid state. A further addition caused the freezing point to rise to a maximum, with approximately 3.5 per cent. of copper, and then to fall gradually. When about 9 per cent. of copper had been added, the cooling curve of the mixture showed a second break after the first freezing point, due to the separation of the copper-silver eutectic. The eutectic arrest, when it first appeared, occurred at a temperature considerably below the average value. The mixture gave only one freezing point when approximately 31 per cent. of copper had been added.

It was evident after the first few determinations that copper is of little use for removing sulphur from silver.

The effect of small additions of copper can only be explained on the principle that part alloys with the silver, whilst the remainder replaces the silver in a portion of the silver sulphide, forming cuprous sulphide which dissolves in the excess of silver sulphide present in the mixture. The initial rise in the temperature of incomplete miscibility is apparently due to the influence of copper in lessening the solubility of the sulphide. This is in

expected since cuprous sulphide is insoluble in copper. The low temperature of the eutectic halt in its early stages may be due to the presence of sulphur in solution.

Microscopic evidence supports the above interpretation, since the amount of sulphide present remains fairly constant until 2 per cent. of copper has been added. A further addition of copper increases the area of sulphide slightly, whilst the addition of more than 3.5 per cent. of copper rapidly removes practically the whole of the sulphide from the silver.

In order to follow the changes a little more completely the effect of heating practically pure silver sulphide with varying percentages of copper was examined to some extent. It was found that the behaviour was very similar to that described above. The mixture separated into two layers in the liquid state, when about 3 per cent. of copper had been added. The freezing point of the layer rich in sulphide was determined in a number of cases. As was to be expected, since cuprous sulphide and silver sulphide form a continuous series of solid solutions when melted together, these freezing points were very poorly defined. The temperature of the freezing point was lowered rapidly by the addition of copper.

On examining these parts of the alloys under the microscope, it was found that the metallic portion of the mixtures had a very considerable solubility, especially in the case of mixtures containing a moderately high percentage of copper.

#### EXPERIMENTAL.

The determinations were carried out in a manner analogous to that described in the previous paper (*loc. cit.*). It was necessary to stir the various mixtures very thoroughly in order to ensure homogeneity.

The following tables give information obtained from the cooling curves.

TABLE I.

*Effect of Copper on Silver containing 13.5 per cent. of Silver Sulphide.*

Alloy number.	Percentage of copper.	First freezing point.	Second freezing point.
—	0	920	903
A.C. 17	0.5	917	908
18	1.0	916	910
19	1.5	915	911
20	2.0	912	—
21	2.8	917	—
22	3.5	917	—
23	4.3	910	—
24	5.2	903	—

TABLE I (continued).

Alloy number.	Percentage of copper.	First freezing point.	Second freezing point.
A.C. 25	6.2	900 <sup>e</sup>	—
26	7.3	892	—
27	9.0	873	752
28	11.9	863	764
29	15.6	840	771
30	19.8	812	768
31	27.1	782	772
32	30.0	773	771
33	37.5	790	771
34	45.6	837	773
35	54.5	867	772

TABLE II.

*Influence of Copper on Silver Sulphide containing 1 per cent. of Free Silver.*

Alloy number.	Percentage of copper.	First freezing point.	Second freezing point.
—	0	802 <sup>e</sup>	—
A.C. 36	0.6	859	798
37	1.2	883	794
39	2.5	898	777
40	3.2	900	766
41	4.0	903	756
43	7.5	918	720
44	10.8	920	674
45	14.1	921	—
46	16.9	921	—
47	19.3	921	—
49	23.2	910	—
50	28.4	892	761
51	33.3	847	770
52	39.9	782	774
53	47.2	803	774

second series of points for alloys A.C. 36 A.C. 41 and every case the freezing points of the layer rich in sulphur. It was found impossible to determine similar freezing points in mixtures containing a higher percentage of copper with any degree of accuracy. So far as could be determined, the freezing point appeared to rise steadily as the percentage of copper was increased.

The compositions of the mixtures tabulated above were determined from the weights of material used, since in the majority of cases there were two liquid layers, and it was found difficult to determine exactly the relative amounts of these.

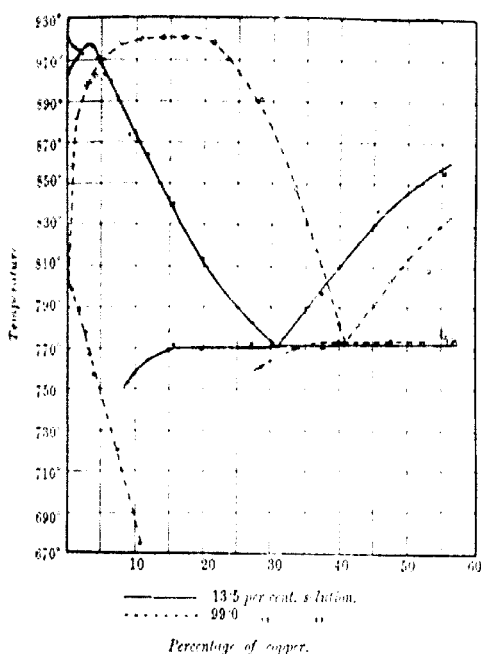
The curves obtained by plotting the above results are shown in Fig. 1.

## II. Influence of Iron on Silver containing Sulphur.

The relation between silver sulphide and ferrous sulphide has been determined by Schoen (*Metallurgie*, 1911, **8**, 737), who found that mixtures of these substances form a simple eutectiferous series, the eutectic containing 11 per cent. of ferrous sulphide, with a melting point of  $615^{\circ}$ .

It appeared highly probable that iron would be a suitable metal

FIG. 1.



to add in order to remove sulphur, since silver and iron are immiscible even at  $1600^{\circ}$  (Petrenko, *Zeitsch. anorg. Chem.*, 1907, **53**, 212), and also ferrous sulphide is stable in comparison with the majority of other sulphides.

In the present investigation the effect produced by adding varying percentages of iron to molten silver containing 11.6 per cent. of silver sulphide has been studied.



Three mixtures only were examined, since these gave sufficient information.

The following table gives the result of the thermal investigation.

TABLE III.

Alloy number.	Percentage of iron.	First freezing point.	Second freezing point.
A.F. 1	0	927°	965
A.F. 2	1.2	951	964
A.F. 3	5.8	960	none
A.F. 4	10	960	none

Alloys after A.F. 1 were found to contain two layers in the solid state. The lower layer was rich in silver, whilst the upper layer was rich in sulphur. The freezing points given refer in all cases to the layer rich in silver. The upper layer in A.F. 4 apparently froze at a temperature above 1000°.

Alloy A.F. 2 contains sufficient iron to saturate half the sulphur present. It will be seen that whilst the first freezing point is raised to 951°, the second freezing point is practically unchanged. It seems probable, therefore, that the iron combines with as much as possible of the sulphur present, and at the same time the sulphide formed is insoluble in silver. Microscopic examination supports this view, since the sulphide remaining in solution in the silver in this alloy behaves in a manner similar to that of silver sulphide, towards etching media. The freezing point, 951°, corresponds with that of an alloy containing 4.5 per cent. of silver sulphide. Apparently, therefore, the ferrous sulphide formed dissolves a considerable portion of the silver sulphide left in the metal. This is made the more probable by the fact that a polished section of the upper layer of the ingot shows traces of a eutectic structure.

Alloy A.F. 3 contains sufficient iron to saturate the whole of the sulphur present. Apparently this is what does occur, since the freezing point of the mixture rises to that of pure silver, and there is no second freezing point. It was found, however, on examining the layer rich in sulphur under the microscope that silver sulphide was present. On adding a considerable excess of iron above that required to saturate the sulphur, the silver present in the upper layer was displaced by iron, the upper layer then consisting of practically pure ferrous sulphide.

Iron, when added to molten silver containing silver sulphide appears to remove the sulphur from solution.

*Effect Produced by Blowing Air through Molten Silver containing Sulphur.*

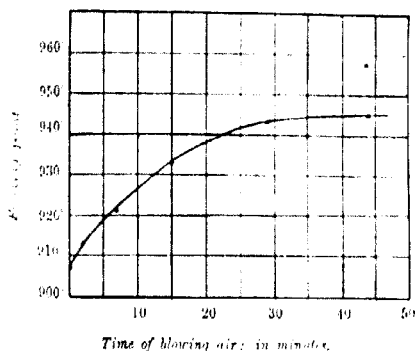
In the experiments being described dry air was blown through molten metal at about 1000°C, the rate being approximately the same in every case.

The alloy contained 16 per cent. of silver sulphide, and 30 grams of alloy were used in each experiment. Table IV gives the results obtained.

TABLE IV.

Experiment number.	Time of blowing air, Minutes.	Freezing point.
1	0	907
2	2	913
3	7	921
4	16	933
5	29	943
6	44	945
7	—	959

FIG. 2.



In experiment 7 the material from experiment 6 was re-melted, charcoal was added, and the mixture was well stirred.

The curve obtained by plotting the results is shown in Fig. 2. It can be seen that the removal of sulphur is somewhat slow under the conditions of the experiments. The rate at which air was blown through the material was of necessity slow, owing to the splashing caused by a rapid stream of gas.

Charcoal was added in experiment 7 to remove the oxygen which was in solution in the silver, in order to determine whether the metal at that stage was pure silver. The freezing point obtained

is slightly lower than that of pure silver. Microscopic examination showed that no sulphide was present. The low freezing point obtained was due probably to the small weight of material used.

I wish to thank Mr. C. T. Heycock for suggesting the work, me, and the Research Fund Committee of the Chemical Society for a grant towards the cost of apparatus.

METALLURGICAL DEPARTMENT,  
CHEMICAL LABORATORIES,  
CAMBRIDGE.

CCLXVI.—*Researches on Silicon Compounds. Part V.  
Preparation of Silicon Tetrachloride, Disilicon  
Hexachloride, and the Higher Chlorides of Silicon  
by the Action of Chlorine on 50 per cent.  
Ferrosilicon, Together with a Discussion on Their  
Mode of Formation.*

By GEOFFREY MARTIN.

THE method once exclusively used for preparing silicon tetrachloride in the laboratory was Oersted's process (*Ann. Chem.*, 1825, [ii], 5, 132) of passing chlorine over a red-hot mass of silica and carbon.

A great improvement was introduced by Gattermann and Weinlig in 1894 (*Ber.*, 1894, 27, 1943; see also Gattermann and Ellery, *Ber.*, 1899, 32, 1114), when they passed chlorine over crude silicon contained in a glass tube heated to 300–310°. They obtained by this process a product containing 80 per cent. of silicon tetrachloride, 20 per cent. of disilicon hexachloride,  $\text{Si}_2\text{Cl}_6$ , 0.5 to 1 per cent. of trisilicon octachloride,  $\text{Si}_3\text{Cl}_8$ .

Up to the present time this has proved by far the easiest method of preparing, not only silicon tetrachloride, but also disilicon hexachloride and the higher chlorides of silicon.

The cost, however, of preparing disilicon hexachloride in quantity by this method is almost prohibitive, and consequently disilicon hexachloride is sold at an extremely high price.

As some kilos. of this costly product were necessary in order to carry out some of the research work on which the author

engaged, it became necessary to devise some cheap and convenient method of preparing disilicon hexachloride in quantity.

After much preliminary work it was found that commercial 50 per cent. ferrosilicon, such as is used for refining steel, can be used instead of the expensive silicon itself for the purpose of preparing disilicon hexachloride in quantity, and that this material forms by far the most economical known method of preparing silicon tetrachloride.

In fact there can be no doubt that, in future, 50 per cent. ferrosilicon must prove the starting point for the preparation of all chlorinated compounds of silicon.\*

Consequently, a description of the method of using this material for preparing silicon tetrachloride, disilicon hexachloride, and the other chlorides of silicon, will be of some value to other workers on silicon compounds, as the optimum conditions were only arrived at after much troublesome experimenting and many preliminary failures.

In order to give some idea of the extent to which the difficulties attached to the preparation of these highly hygroscopic liquid chlorides of silicon were overcome by means of the final form of apparatus described below, the author may state that he succeeded in isolating 3 kilos. of pure disilicon hexachloride, 200 grams of trisilicon octachloride, and more than 54 kilos. of pure silicon tetrachloride by passing 143 kilos. of chlorine over 50 kilos. of ferrosilicon. This was done in an ordinary chemical laboratory, and all leakage of chlorine and of the volatile silicon tetrachloride was so completely overcome in the final stages of this preparation that ordinary class work went on around the apparatus while the preparation was actively proceeding.

Since water causes the instant decomposition of these chlorides, all traces of atmospheric moisture must be carefully excluded from all parts of the apparatus, and it is this necessity that makes their preparation a matter of so much trouble.

The large amount of disilicon hexachloride prepared by this process enabled the author to obtain it in a state of very great purity, and so he was able to investigate its properties more carefully than was possible with earlier workers. It was found, for example, that Gattermann and Weinlig's value for the boiling point of disilicon hexachloride,  $\text{Si}_2\text{Cl}_6$ , namely,  $145-146^\circ$ , was undoubtedly a little too high, the true boiling point being  $141-145.5^\circ/760$  mm. The boiling points of the substance under

\* The silicon purchased as 50 per cent. ferrosilicon is nearly eighteen times cheaper than when purchased as pure silicon; moreover, 50 per cent. ferrosilicon is readily available, the other grades being made only on the small scale.

pressures ranging from 12 mm. to ordinary atmospheric pressure were also accurately determined. They are tabulated on page 2842.

The density of pure disilicon hexachloride was found to be  $D_4^{20}$  1.5624; Troost and Hautefeuille gave  $D$  1.58.

The refractive index for sodium light ( $D$  line) was found to be 1.4748 at  $18^\circ$ . Gattermann and Weinlig (*loc. cit.*) give the refractive index for "red light" as 1.45.

It was also shown that although at the ordinary temperature disilicon hexachloride does not combine with chlorine (although the latter is very soluble in it), yet at about  $300^\circ$  it takes up this gas and burns to silicon tetrachloride, thus,  $\text{Si}_2\text{Cl}_6 + 2\text{Cl}_2 = 2\text{SiCl}_4$ .

This is a new fact of considerable importance, since it throws light on the mode of formation of disilicon hexachloride by the action of chlorine on silicon or ferrosilicon (see below).

Although Gattermann and Weinlig (*loc. cit.*) showed that when water acts on disilicon hexachloride there is produced silicic acid,  $(\text{SiO}_2\text{H})_2$ , yet they seem to have overlooked the fact that there are also soluble colloidal forms of silico-oxalic acid produced at the same time, as the author proved in the course of this work. These colloidal forms are to be investigated.

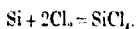
After the disilicon hexachloride had distilled, about 200 grams of crude trisilicon octachloride passed over. This, after careful fractionation, yielded about 150 grams of pure octachloride, which boiled at  $210\text{--}213^\circ$  under atmospheric pressure (Gattermann and Weinlig, *loc. cit.*, give  $210\text{--}215^\circ$ , and Besson and Fournier, *Compt. rend.*, 1909, **148**, 840, give  $215\text{--}218^\circ$ . This value is undoubtedly too high). However, it was shown that trisilicon octachloride gradually decomposed when distilled under the ordinary pressure, giving rise to a dark-coloured residue. To avoid decomposition it was found advisable to distil it under diminished pressure. It could be repeatedly distilled without decomposition at pressures below 110 mm. (when it boiled at about  $149^\circ$ ). Trisilicon octachloride is considerably less stable than disilicon hexachloride. The density  $D_4^{20}$  1.61, and the refractive index ( $D$  line) 1.5135 at  $14.5^\circ$ .

After the trisilicon octachloride had been removed the liquid remaining was fractionated under greatly diminished pressure, and higher chlorides were isolated in small quantities. These were decomposed by water, giving rise to white, amorphous products which dissolved in alkalis with the evolution of hydrogen. A later communication will be made on this subject. Besson and Fournier (*Compt. rend.*, 1909, **148**, 839; **149**, 34) recently described higher chlorides, which were isolated by a different method.

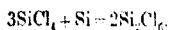
The residues left after removal of these chlorides consisted of (a) about 13 grams of a viscid, black, tar-like mass and (b) about 20 grams of a black powder like animal charcoal. These products are now being investigated.

It is thus shown that the product obtained by the action of chlorine on silicon and ferrosilicon is no simple substance, but a very complex mixture of silicon compounds, the different components of which are now in process of isolation.

Gattermann and Weinlig (*loc. cit.*) explained the formation of disilicon hexachloride when chlorine passes over silicon at 300° by assuming that the chlorine first directly unites with the silicon to form silicon tetrachloride, thus:



and they supposed that the silicon tetrachloride thus formed at once reacts with more silicon to produce the hexachloride, thus:



In the last twenty years this explanation of Gattermann and Weinlig has been universally accepted as the correct one. However, this explanation is certainly quite erroneous for the simple reason that the low temperatures employed by Gattermann and Weinlig, and also by the author in the preparation of disilicon hexachloride from the action of chlorine on ferrosilicon, silicon tetrachloride does not react with silicon to produce disilicon hexachloride in noticeable quantity. This is conclusively shown in the experiments quoted above. Gattermann and Weinlig made not the slightest attempt to verify their theory experimentally. Indeed, on theoretical grounds the formation at a low temperature of disilicon hexachloride from silicon and silicon tetrachloride would appear to be most improbable, since disilicon hexachloride is an endothermic compound, and its formation requires the absorption of a considerable amount of heat.

A white heat would favour its formation (as in the similar case of ceric oxide), but a low temperature would not be expected to act in this way. Troost and Hautefeuille showed that at a temperature reaching the fusing point of porcelain (that is, at a white heat) the formation of disilicon hexachloride from silicon and silicon tetrachloride does take place to a limited extent (*Ann. Chim. Phys.*, N. S., 7, 459), but the conditions under which the formation takes place in Troost and Hautefeuille's experiments are entirely different from those under which it occurs in Gattermann and Weinlig's experiments, where the temperature is kept quite low, and in the author's experiments, whereby disilicon hexachloride is obtained by the action of chlorine on ferrosilicon, where also only

low temperatures are employed, so that arguments derived from Troost and Hautefeuille's experiments do not apply in any way to the case now under consideration.

The problem to be explained is how a large proportion, amounting to something like 20 per cent. of disilicon hexachloride, is produced by the action of chlorine on silicon at the low temperatures (about  $300^{\circ}$ ) employed by Gattermann and Weinlig.

The conclusive refutation of Gattermann and Weinlig's theory is given by the following experimental facts established by the author.

(1) When silicon tetrachloride is distilled over either silicon or ferrosilicon heated to any temperature between  $200^{\circ}$  and  $540^{\circ}$ , no noticeable amounts of disilicon hexachloride can be detected in the resulting silicon tetrachloride; in other words, disilicon hexachloride is not formed by the action of silicon tetrachloride on silicon at moderately low temperatures, as Gattermann and Weinlig supposed.

(2) Silicon tetrachloride was prepared by allowing chlorine to act on ferrosilicon at one end of a long tube packed with ferrosilicon, and the silicon tetrachloride thus produced was passed over the long length of heated ferrosilicon in the later part of the same tube. Less disilicon hexachloride was found to be present in the resulting silicon tetrachloride than when only short lengths of ferrosilicon were used. According to the Gattermann and Weinlig theory, the longer the length of ferrosilicon traversed by the vapour of the silicon tetrachloride the better would be the opportunity for the reaction,  $3\text{SiCl}_4 + \text{Si} = 2\text{Si}_2\text{Cl}_6$ , to proceed, so that an increased yield of disilicon hexachloride should have resulted.

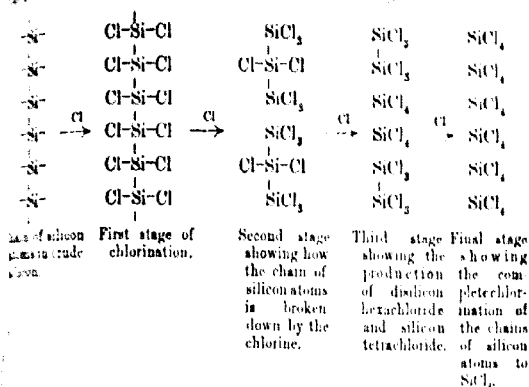
(3) Moreover, the lower the temperatures employed the lower the yield of disilicon hexachloride. For example, when the tubes containing ferrosilicon were kept at  $180^{\circ}$ – $200^{\circ}$ , in some cases more than 8.6 per cent. of disilicon hexachloride was produced; at  $250^{\circ}$ – $260^{\circ}$  about 4.6 per cent., whilst at  $300^{\circ}$ – $310^{\circ}$  only about 4 per cent. was obtained. This should not be the case if Gattermann-Weinlig theory be correct.

It is therefore obvious that some other explanation of the formation of disilicon hexachloride and trisilicon octachloride must be sought for.

The theory now advanced, which explains all the known facts in a satisfactory manner, is the following:

Ordinary silicon (and also the metallic silicides) consists of complex chains of silicon atoms directly united together. The first action of chlorine on silicon (or metallic silicides) is, consequently, a complex one. The chain of silicon atoms is

immediately disrupted by the chlorine, but there are first produced complex chlorinated products still containing chains of silicon atoms directly united. These complex chlorides are then attacked by more chlorine, and decompose into simpler chlorides, such as  $\text{Si}_2\text{Cl}_6$ ,  $\text{Si}_3\text{Cl}_{12}$ ,  $\text{Si}_4\text{Cl}_{16}$ ,  $\text{Si}_5\text{Cl}_{20}$ , and  $\text{Si}_6\text{Cl}_{24}$ , all of which have been isolated. Lastly, the chlorine then attacks these products and produces therefrom silicon tetrachloride. Thus silicon tetrachloride is not the first product of chlorination (as Ostermann and Weinlig supposed), but rather is the final product of chlorination, as indicated in the following scheme:



Consequently, silicon tetrachloride is the main product of the reaction, but small quantities of complex chlorides still containing directly linked silicon atoms remain in the silicon tetrachloride, thus indicating its mode of origin.

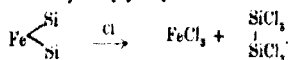
The amount contained in the silicon tetrachloride of disilicon hexachloride, which possesses only two silicon atoms directly linked, is much greater than the amount of chlorides containing longer chains of silicon atoms, such as trisilicon octachloride, because the longer chains of silicon atoms are the first to be broken under the further action of the chlorine.

The same considerations apply to the case of the metallic silicides, and the fact that silicides, such as 50 per cent. ferro-silicon, can be used for preparing disilicon hexachloride and higher chlorides containing directly linked silicon atoms (see above), may be taken as evidence that in these metallic silicides chains of directly linked silicon atoms are present, and that the small amounts of higher chlorides containing directly linked silicon atoms produced in their chlorination contain parts of the unbroken chains of silicon atoms which were originally present in these



silicides, but which have been for the most part broken down by the further action of chlorine, into silicon tetrachloride.

The formation of disilicon hexachloride from ferrosilicon, for example, would be very simply explained thus:



The fact seems definitely established that many of these compounds, such as ferrosilicon, are simply mixtures of complex silicides, and in many cases there is reason to believe that the silicides are "compounds" at all, but are merely solid solutions of iron in silicon.

The following facts are in favour of this view of the nature of the higher chlorides of silicon:

(1) Complex chlorides of silicon are invariably produced when chlorine acts on silicon or silicides, but (as shown above and below) their formation cannot be accounted for by the action of chlorine on silicon tetrachloride.

(2) That the disruption in the presence of chlorine of the linked silicon atoms, such as exist in disilicon hexachloride, into silicon tetrachloride does actually take place was proved by passing vapours of disilicon hexachloride mixed with chlorine through a tube heated to about 300°, when the disilicon hexachloride was burnt and burnt to silicon tetrachloride, thus:  $\text{Si}_2\text{Cl}_6 + \text{Cl}_2 \rightarrow \text{SiCl}_4$ . It was also proved that at the ordinary temperature disilicon hexachloride does not combine with chlorine to form silicon tetrachloride.

It is therefore practically certain that the small amounts of silicon hexachloride, octachloride, etc., found in the silicon tetrachloride produced by chlorinating silicon or ferrosilicon, are simply the residue or debris of much larger quantities of silicon hexachloride or octachloride originally present, this residue having escaped destruction by the chlorine present owing to the fact that it was quickly removed from the sphere of action of the chlorine by quick cooling.

(3) This theory also accounts satisfactorily for the fact that the lower the temperature at which chlorine acts on ferrosilicon, the greater is the yield of disilicon hexachloride and other chlorides of silicon containing chains of directly united silicon atoms in the molecule.

On the Gattermann-Weinlig theory the reverse effect would rather be expected to take place.

(4) Next to carbon, silicon is the element having the most highly developed power of self-combination. Elementary silicon, therefore, cannot be regarded as a mere aggregate of single Si

but rather the element must be thought of as composed of complex molecules consisting of many silicon atoms directly united together, possibly in rings or chains, as in the case of carbon. It would therefore, appear to be unreasonable to suppose that at the moment the chlorine atoms act on these molecules they immediately fly to pieces with the production of single atoms of silicon, which are then acted on by the chlorine to produce silicon tetrachloride. It is more reasonable to suppose that the chlorination takes place slowly and the whole complex silicon molecule is attacked, forming first complex chloro-compounds, which later, by the further action of the chlorine, break down into simple molecules, the end-product of the whole complex chain of events being silicon tetrachloride. In this connexion there is the curious experimental fact (see p. 2847) that when chlorine is passed over ferrosilicon heated to a suitable temperature, the formation of silicon tetrachloride does not begin at once. First of all, a period elapses (which may last any time from thirty minutes to one hour, even under special and not well understood conditions, to three hours) during which no silicon tetrachloride at all passes over, but in which it is possible that the surface of the ferrosilicon is being acted on with the production of complex chlorinated silicon compounds, by the further chlorination of which the silicon tetrachloride is produced.

Once this initial stage is over, the formation of silicon tetrachloride takes place with great rapidity.

#### EXPERIMENTAL.

*Preliminary Experiments.*—Some preliminary experiments were carried out by placing 50 per cent. ferrosilicon in glass tubes and passing chlorine through them while the latter were heated to various temperatures in a Gattermann's bomb furnace.

At first a temperature of 300–310° was maintained. It was soon found, however, that glass tubes were quite unsuitable for use with ferrosilicon. In the first place, the ferric chloride produced by the chlorination of the iron sublimed down the tube, where it caused it to block up, and the tubes usually broke when they were cleaned out. Moreover, unless the stream of chlorine is carefully regulated, the temperature of the reaction may rise so high that the glass may fuse at certain points.

The use of glass tubes, therefore, was abandoned in favour of ordinary iron gas-piping, 30 mm. bore, fitted at the end with ordinary corks. It was found that the iron piping was soon burnt through by the chlorine at that end of the tube where the chlorine entered and began to react with the ferrosilicon. The expedient

of placing the ferrosilicon on movable iron troughs inside the tube, was tried, but was abandoned, as the troughs stuck firmly to the inside of the tube (owing to the ferric chloride acting as a cement), and the latter could not be effectively cleaned out.

Although, when the temperature of the furnace was maintained at  $300^{\circ}$ – $310^{\circ}$ , the iron tube was very rapidly attacked by chlorine, it was found that by employing a lower temperature the corrosive action of the chlorine was very much diminished. A temperature of  $180^{\circ}$ – $200^{\circ}$  was found to be very suitable. A temperature of  $170^{\circ}$  caused the action of the chlorine on the ferrosilicon to become so slow that it was abandoned in favour of the higher temperature. Moreover, by keeping the temperatures low, the yield of disilicon hexachloride (the substance it was desired to obtain in quantity) was practically doubled. Thus in the initial experiments when the furnace was maintained at  $300^{\circ}$ – $310^{\circ}$ , the yield of disilicon hexachloride in the crude silicon tetrachloride was about 1 per cent.

When the furnace was kept at  $250^{\circ}$ – $260^{\circ}$  the yield of disilicon hexachloride rose to 4.6 per cent., whilst at  $180^{\circ}$ – $200^{\circ}$  the yield rose to 8.6 per cent. At  $170^{\circ}$  the action of chlorine on ferrosilicon took place too slowly for effective work.

#### *Apparatus for the Production of Silicon Tetrachloride and Disilicon Hexachloride in Quantity.*

As the result of these preliminary experiments an apparatus for producing silicon tetrachloride in quantity was built up. In chlorine from a cylinder was dried by passing through sulphuric acid, and then, by means of a T-piece, was led alternately through two iron tubes set in a Gattermann bomb furnace and charged with ferrosilicon. The ends of the tubes were fitted with ordinary corks through which glass leading-tubes passed.

The corks were best coated with paraffin-wax or bakelite varnish. A plug of glass wool at the far end of the tubes arrested the ferric chloride, which slowly distilled down the tube, and tended to block up the leading tubes. The silicon tetrachloride was collected in a Winchester bottle.

This apparatus worked well for the production of a few kilos. of silicon tetrachloride and a few hundred grams of disilicon tetrachloride. When, however, it became necessary to prepare about 50 kilos. of silicon tetrachloride, so that about 3 kilos. of disilicon hexachloride could be isolated therefrom, grave defects were revealed in the apparatus.

In the first place the corks needed constant replacement or repair even when well coated with bakelite varnish. Moreover, they often become impregnated with disilicon hexachloride and to

higher chlorides, which on contact with atmospheric moisture soon decomposed with the production of explosive silicon oxy compounds. Consequently, the corks, after a time, became unpleasant to handle, due to forcing them into or withdrawing them from the tube stoppers occurred, which, when much disilicon hexachloride had accumulated, could cause injury to the hands. It should be noted that all these compounds of silicon which contain silicon atoms directly united in the chain are, apparently, formed with the application of heat, and so are capable of explosion under suitable conditions.

Frequently in the course of the experiment the corks blew off without warning with considerable violence, either as the result of sudden blockage in the tube by the sublimed ferric chloride, or, rarely, on certain occasions, by the presence of excess of chlorine apparently causing the ignition of the higher chlorides formed in the tube (see p. 2859).

Leakage of chlorine from the corks could only be prevented with great difficulty, and as about 143 kilos. of chlorine were required for the production of the amount of silicon hexa- and tetra-chlorides used, the leakage of chlorine became serious. It was, therefore, essential to devise chlorine-tight end-pieces, and after some experimenting, the corks were finally displaced by detachable iron caps screwed on to the ends of the tubes.

The threads were made gastight at first by the use of ordinary red wax (which acted admirably as a lute for chlorine), but as the fibres of asbestos introduced into the threads were found not better. The difficulty of chlorine leakage was thus surmounted, and the ends of the tube could be screwed off with ease, the tube withdrawn, washed out, and recharged when this was necessary.

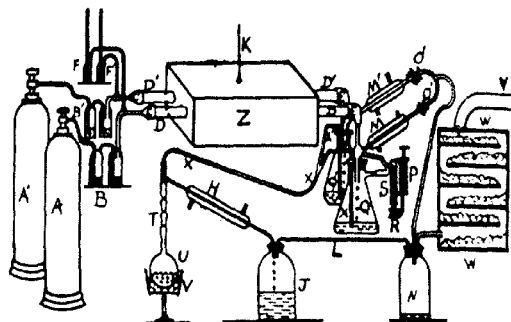
Since blockages in the tubes invariably occurred after a certain period of time, explosions could easily arise unless the pressure existing inside the tubes was properly controlled. This was done by attaching mercury manometers to the mouths of the tubes, any rise of pressure inside the tubes being indicated by the rise of mercury in these manometers, which also acted as safety valves.

Lastly, it was necessary to absorb chlorine and other corrosive gases which passed through the apparatus. This was very efficiently done by means of a lime absorber. It consisted of a wooden box, 100 cm. long by 70 cm. wide, fitted with shelves so shaped that the chlorine passed over them in a zigzag fashion. The waste gas entered at the bottom, and escaped into the flues at the top through holes of about 3 cm. diameter bored in the shelves. The gas had to be changed every week, the face of the box being so built up.

arranged that the front opened like a door, so that the whole could be cleaned out when necessary. The box was made absolutely tight by luting with ordinary yellow soap. The complete apparatus is shown in Fig. 1. *A* and *A'* are two chlorine cylinders, each holding about 42.5 kilos. of liquid chlorine. *B* and *B'* are two series of sulphuric acid wash-bottles, whilst *D* and *D'* are two 3-cm. gas-pipe iron tubes, about 120 cm. long, fitted with leading pipes attached to iron screw-on caps, *C* and *C'*. *F* and *F'* are the two mercury manometers attached by means of glass and rubber tubing to the leading tubes of *D* and *D'*, so that the pressures prevailing inside the pipes *D* and *D'* are accurately known, an increase of pressure being indicated by the rise of mercury in *F* and *F'*.

The mercury in the reservoirs of *F* and *F'* is covered with a

FIG. 1.



of concentrated sulphuric acid, which protects the mercury to a large extent from vigorous attack by the chlorine gas. *Z* is a Gerhardt bomb furnace, the internal temperature of which is indicated by the thermometer *K*. In these experiments the temperatures kept on the average between 180° and 200°. The tubes *B* and *B'* end in iron screw-on elbow joints *E* and *E'*, from which a 3-cm. iron pipe of 12 mm. bore projects into the two receiving vessels *Q* and *Q'*. These consisted of two 2-litre filter-flasks, in which almost all the crude silicon tetrachloride passing over from the apparatus condensed, only a very small amount passing on through the condensers *M* and *M'* and collecting in the bottle *N*.

An air-pump *P* provided with a mercury trap *R* and a delivery tube *S* is directly united to the flasks *Q* and *Q'*, and by forcing air into *Q* and *Q'* (after closing sundry clips controlling the exits from

the flask) the crude silicon tetrachloride could be forced up the tubes  $X$  and  $X^1$  (which reach almost to the bottom of the filter-funnels  $Q$  and  $Q^1$ ), along the pipe  $XX$  into the fractionating column  $T$ , and thus into the fractionating flask  $U$ , which is heated on a water-bath  $V$ .

The fractionating column employed was a Young's three bulb separator still-head, which was fused on to a litre flask. The rising tube from the top of the distilling column  $T$  passes through condenser  $H$  into a receiver  $J$  (a Winchester bottle). From  $J$  a rising tube  $L$  runs to the catch-bottle  $N$ , and thence a wide leading tube runs to the lime absorber  $W$ . Here any chlorine and silicon tetrachloride vapours enter at the bottom, and after circulating over the lime on shelves in zigzag fashion, escape at the top to the flues. The absorption of chlorine and silicon tetrachloride in the apparatus was almost complete.

The iron piping was packed with coarsely crushed ferrosilicon, which commenced a few cm. in front of the place where the tubes enter the furnace, and extended for some 20 to 30 cm. down the tube, about 1 to 2 kilos. of ferrosilicon being used for each charge. A short length of ferrosilicon was found advantageous in that chlorine was found to be completely absorbed by the short pieces, and a longer length only tended to cause the tube to block owing to the sublimed iron chloride condensing in the ferrosilicon at the far end of the tube. With short lengths of packing considerable space was left in which the iron chloride could condense without choking the tube.

The method of working the apparatus was as follows: The tubes  $XX$  and  $DD^1$  were charged with ferrosilicon, placed in the furnace, and their temperature was raised to  $180-200^\circ$ , the temperature indicated by the thermometer  $K$ . Chlorine was then admitted as a moderately rapid stream, the rate being controlled by the stop-cocks attached to the cylinders  $A$  and  $A^1$ .

The action does not take place immediately. Usually the silicon tetrachloride begins to pass over in about thirty minutes after starting the operation. Occasionally, however, it was found that four's, two hours', and in some cases three hours' passage of the gas through the heated tube was necessary before the silicon tetrachloride began to pass over in quantity.

Temperature did not seem to play a great part in shortening the time of this preliminary period, as even when the furnace was heated at as high a temperature as  $300-310^\circ$  the same phenomenon was observed, and keeping the temperature at  $190-200^\circ$  did not cause a sensible prolongation of this period of waiting before the silicon tetrachloride began to pass over. Also a very

rapid initial stream of chlorine did not shorten sensibly the reaction period.

This effect is, possibly, due to the fact that the chlorine has time to attack the surface of the ferrosilicon and produce intermediate complex silicon chlorinated compounds before the production of silicon tetrachloride takes place. When, however, the reaction started it took place moderately rapidly with a considerable rise of temperature, and the silicon tetrachloride passed over in a steady stream and collected in the vessels *Q* and *Q'* as a yellow, oily liquid.

The tubes are worked for about three hours at a time, and simultaneously or alternately, but as a rule matters were arranged that one tube was in full action whilst the other one was being pulled out and re-charged. The silicon tetrachloride condensed in the filter-flasks *Q* and *Q'*, and was from time to time forced by the pressure of the chlorine from the cylinders *A* and *A'* through pipes *X* and *X'* into the fractionating flask *U*. When this was done the screw clips were once more opened and the action continued. When, for any reason, it was inconvenient to use the pressure of the chlorine from the cylinders *A* and *A'* for forcing the liquid from *Q* into *U*, air-pressure applied by the air-pump was used for this purpose.

The silicon tetrachloride collecting in *U* was then fractionally distilled, the distillate being collected in the Winchester bottle *J* when filled is removed and replaced by another Winchester bottle. The silicon tetrachloride is stored in these bottles with ordinary corks well boiled in paraffin wax, the corks being taken out of the paraffin bath and while still warm being forced into the neck of the bottle, and covered over with a layer of melted paraffin, so as to prevent any danger of atmospheric moisture reaching the silicon tetrachloride. When sealed in this way the silicon tetrachloride can be stored for months without depreciation.

When the flask *U* became nearly full of residues of high boiling point, the water-bath was replaced by an oil-bath heated to a higher temperature.

The disilicon hexachloride passed over at 147–149°, and was collected separately and fractionated in a separate flask, also provided with a fused-on Young evaporator still-head. There was thus left behind in *U* a gradually increasing amount of residues of high boiling point, which were later proved to consist of higher chlorides of silicon (see below), besides a mass of tarry material and a black, solid residue, much like animal charcoal in appearance.

*Method of Charging and Discharging the Tubes.* When a quantity

observed that the supply of silicon tetrachloride dropping into  $Q$  or  $Q'$  from one of the tubes diminished, or when the pressure in the tube began to increase rapidly (as indicated by the manometers  $F$  or  $F'$ ), it was known that either the tube was becoming exhausted, or that it was becoming choked up by sublimed ferric chloride. This occurred, on the average, every three hours. Consequently, it became necessary at the end of this time to withdraw the tube, clean it out, recharge it with ferrosilicon, and replace it in the furnace.

To do this, the supply of chlorine is cut off from the tube, then the end caps  $C$  and  $E$  are rapidly unscrewed (these caps are cold enough to be touched by the hand, since they project nearly 30 cm. from the furnace), the tube is drawn out over iron rollers (not shown in the illustration), then, while hot, rapidly transferred to a sink. A cork fitted with a leading tube is attached to one end (after first withdrawing the plug of glass wool), and a supply of cold water allowed to flow into the tube. This water, entering the tube, is soon heated to boiling, and largely converted into steam, which blows the contents of the tube through the opening of the tube and effectively and rapidly cleans out the ferric chloride in the tube. The stream of cold water is allowed to flow through the tube until it runs clear, when the ferric chloride has been completely removed. The iron rod with a pointed end is then applied to clear out any particles of ferrosilicon still adhering to the tube, and the wet, clean tube is then transferred to a combustion furnace and dried by heating, while a current of air is blown through it. The tube is then removed from the combustion furnace, rapidly charged with 50 per cent. ferrosilicon, as described on page 2847, and replaced in the furnace (being run in over the rollers above-mentioned), the caps at  $C$  and  $D$  are screwed on, and the stream of chlorine is once more let into the apparatus.

As each iron tube corroded very rapidly just at one point, namely, at the end where the chlorine enters and acts on the ferrosilicon, in recharging care was taken to place the charge at the end of the tube opposite to that end previously used, so that the erosion should take place equally at each end. However, even with this precaution, the average life of each iron tube was not more than six experiments, the chlorine burning a hole through the iron piping at the point where the action was most intense.

The 50 per cent. ferrosilicon washed out of the tube is well washed with water until free from iron chloride, dried in an air-bath, and once more was used for recharging a second tube. The ferrosilicon was thus used over and over again until consumed.



At the same time considerable wastage occurred, owing to portions of the ferrosilicon escaping as a suspension in the washing water.

Too finely powdered ferrosilicon was found not to be suitable for use, as blockages in the tube were thereby easily occasioned.

Since traces of higher chlorides accumulate at the end of the tube and are converted by the washing water into explosive compounds, these, on striking with the iron rod or on scraping, may explode if in considerable amount, so that a certain amount of care must be taken not to allow these residues to accumulate to any great extent in the tubes.

This apparatus, which was gradually evolved out of repeated failures and mishaps, worked very smoothly and efficiently and by means of it about 54 kilos. of silicon tetrachloride were prepared by the passage of 143 kilos. of chlorine gas over about 50 kilos. of 50 per cent. ferrosilicon.

From the crude silicon tetrachloride, which was distilled as fast as it was produced in the continuous fractionating apparatus there were produced about 3 kilos. of disilicon hexachloride and about 500 grams of residues which contained nearly 200 grams trisilicon octachloride.

#### *Apparatus for Distilling the Crude Silicon Tetrachloride and to Separate the Higher Chlorides.*

The problem of dealing with large quantities of the highly volatile silicon tetrachloride (b. p.  $59^{\circ}$ ) is complicated by the fact that atmospheric moisture decomposes it, with the formation of hydrochloric acid and the deposition of silicic acid.

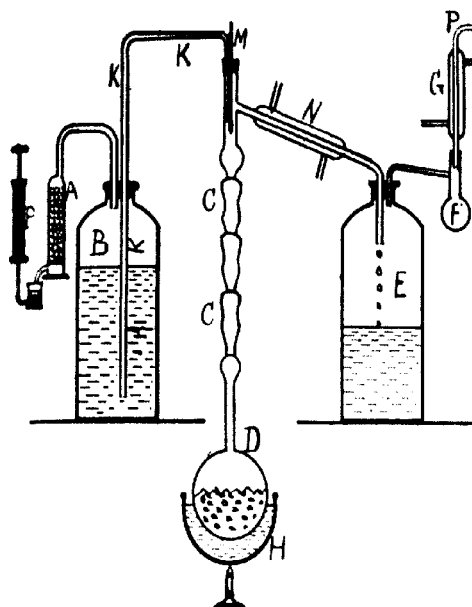
Consequently, all the vessels in which the liquid is kept must be most carefully dried before allowing the silicon tetrachloride to enter.

A description of the apparatus used for distilling and fractionating this silicon tetrachloride in the absence of atmospheric moisture may prove useful to other workers, as the final form was arrived at only after much troublesome experimenting. The apparatus finally used is shown in Fig. 2.

A is a vessel filled with coarsely granulated calcium chloride. To this vessel an air-pump, *P*, is attached, connexion being made through a mercury trap, *T*, to prevent the silicon tetrachloride vapours reaching the pump. By this means dry air can be forced into the Winchester bottle, *B*, containing the crude silicon tetrachloride to be distilled. As a result of this increased air pressure the crude silicon tetrachloride is forced up the tube *KK* into the fractionating flask *D*, which is fitted with a Young's three-necked evaporator still-head, *C*, fused on to *D*. At the top of the still-

and *C* is a thermometer, *M*. The leading tube from the still-head passes through a condenser, *N*, as shown. The flask *D* is placed on a water-bath, *H*, and after the proper amount of crude silicon tetrachloride has been forced into *D* from the reservoir *B*, *x* is fractionated, the residual disilicon hexachloride (b. p. 145°), together with the higher chlorides, remaining behind in *D*, whilst the volatile silicon tetrachloride (b. p. 59°) passes up the column *C* and, condensing in *N*, runs into the receiver *E*. *F* is a catch

FIG. 2.



for any silicon tetrachloride vapour that does not condense in *E*, *G* being an auxiliary condenser. In hot weather *F* should be immersed in ice. *P* leads out to the flues.

The bottle *B*, the distilling column *C*, the bottle *E*, and the flask *F* are all fitted with corks which have been boiled in paraffin oil.

By means of this apparatus many kilos. of silicon tetrachloride can be continuously distilled free from contact with atmospheric moisture, and separated from the residues of high boiling point, which thus accumulate in the flask *D*.

As the liquid concentrates in *D* it becomes dark brown and black, whilst the liquid in *E* consists of almost pure silicon tetrachloride containing a little dissolved chlorine. It is of a yellowish colour, but can be rendered colourless by allowing it to remain for some days in contact with freshly-ignited animal charcoal, followed by redistillation.

When a sufficient quantity of residues has collected in *D*, the water-bath, *H*, is replaced by an oil-bath, and the residues are distilled, the bulk of the material passing over (after the silicon tetrachloride has been removed) at  $147\text{--}148^\circ$  under the ordinary atmospheric pressure. There remains in *D* some black solid residues, and a black powder resembling animal charcoal.

#### *Redistillation of the Crude Disilicon Hexachloride.*

The crude disilicon hexachloride distilled, as above described, from the residues was now purified by keeping it over freshly ignited animal charcoal, and was then fractionally distilled in an apparatus made entirely of glass, the fractionating column employed being a Young's three-bulb evaporator still-head fused to the flask. During this operation the most rigorous precautions had to be taken to dry most thoroughly all the vessels used in the distillation, otherwise a turbid distillate would result.

Ordinary drying by washing out with alcohol followed by ether and blowing warm air through the apparatus was not efficient enough. The flasks had to be heated nearly to redness (after a preliminary washing with alcohol and ether), and then, after blowing out with hot air, must be attached still fairly hot to the receiver. The pure substance boils at  $144\text{--}145.5^\circ/760$  mm. The boiling point,  $145\text{--}146^\circ$ , given by Gattermann and Weinlig (*loc. cit.*) is undoubtedly a little too high. The boiling points under diminished pressures were also determined as follows:

#### *Boiling Points of Disilicon Hexachloride.*

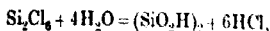
Pressure. mm.	B. p.	Pressure. mm.	B. p.	Pressure. mm.	B. p.
12	40 <sup>1</sup>	41	61 <sup>2</sup>	130	94
12.5	43	50	65	135	96
13	46	53	66	140	98
14	47	90	80	150	99
17	48.5	95	81	181	104
19	49	105	84	195	106
20	50	110	86	200	107
22	53.5	119	89	222	109
27	56	122	90	760	144 <sup>1</sup> 145 <sup>2</sup>
31	60	126	91		

The pure substance froze to a white, ice-like mass at  $-3^\circ$ , which did not finally melt until a temperature of  $-1^\circ$  was reached.

The density of disilicon hexachloride determined with 200.6684 grams was found to be  $D_4^{20}$  1.5624. Troost and Hautefeuille gave 1.58 at 0°.

The refractive index for sodium light ( $D$  line) as determined by the hollow prism method was found to be 1.4748 at 18°. Another determination by a drop method gave 1.4775 at 14.5°. Gattermann and Weinlig gave the refractive index for "red light" as 1.45.

Although Gattermann and Weinlig showed (*loc. cit.*) that when water acts on disilicon hexachloride, silico-oxalic acid is produced, 1245:



in the form of a white precipitate, insoluble in acids, but soluble in alkalis with the evolution of hydrogen, yet it seems to have escaped their notice that soluble colloidal forms of silico-oxalic acid are produced at the same time. This was proved as follows: disilicon hexachloride was treated with a little water, when a white precipitate of silico-oxalic acid separated, which was collected. The residual clear liquid, however, still contained some silico-oxalic acid in colloidal solution, as was proved by adding to the liquid a few drops of concentrated ammonia solution, when a considerable gelatinous precipitate was obtained. This colloidal form of silico-oxalic acid is now being further investigated, and an account will be given in another paper.

*Analysis of Disilicon Hexachloride.*—By means of a small pipette made of a piece of small-bore glass tubing drawn out at one end and fitted with a rubber teat at the other end (the whole pipette being most carefully dried before use), 1.3029 grams of disilicon hexachloride were transferred to a dry weighing bottle, exactly weighed, and then decomposed by water rendered alkaline with ammonia. The contents of the weighing bottle were finally rinsed out, the precipitated silicic acids collected, the washings exactly neutralised with nitric acid and titrated with silver nitrate, using potassium chromate as indicator. (Found, Cl, 78.9. Calc., Cl, 78.9 per cent.)

#### *Isolation and Properties of Trisilicon Octachloride, $\text{Si}_3\text{Cl}_8$ .*

After the crude disilicon hexachloride had been distilled over, there remained in the flask a dark-coloured mass, consisting of liquid and solid. The liquid was poured into a fractionating flask, and there remained a black, amorphous powder resembling animal charcoal, and weighing 160 grams. This powder is undergoing examination.

The black liquid, weighing about 377 grams, was now distilled,

using a rod-and-disk fractionating column fused on to the flask, and heating on a metal bath.

After separating the disilicon hexachloride still in the flask between  $141^{\circ}$  and  $147^{\circ}$  (atmospheric pressure), the temperature rose rapidly to  $170^{\circ}$ , and then more slowly to  $185^{\circ}$ . The weight of the fraction boiling at  $141$ – $185^{\circ}$  was 128 grams.

The temperature then rose rapidly from  $185^{\circ}$  to  $200^{\circ}$ , when the receiver was again changed, 64 grams distilling between  $185^{\circ}$  and  $200^{\circ}$ . The bulk of the liquid, amounting to 185 grams, passed over, however, at  $200$ – $220^{\circ}$ , a large portion of which distilled at about  $215$ – $217^{\circ}$ .

There remained in the flask about 20 c.c. of a dark-colored liquid boiling at above  $220^{\circ}$ , which was worked up separately (see below).

The distillates, which consisted of yellow, fuming liquids, were now subjected to careful fractionation under diminished pressure, using a 21 rod-and-disk fractionating column fused on to a glass flask, and heating from an oil bath. The liquids were again separated into some disilicon hexachloride and trisilicon octachloride, the latter being obtained pure after one or two fractionations. The amount of pure trisilicon octachloride was about 77 grams, about 30 grams of impure liquid being simultaneously isolated.

The published accounts of the boiling point of this substance vary considerably. Thus, Gattermann and Weinlig (*loc. cit.*) give  $210$ – $215^{\circ}$ , whilst Besson and Fournier (*loc. cit.*) give  $215$ – $22^{\circ}$ . There is no doubt, however, that Besson and Fournier's product was not pure. The boiling point of the above product is  $210$ – $213^{\circ}$  under the atmospheric pressure, agreeing closely with Gattermann's value. The substance slowly decomposes when boiled under the ordinary pressure, giving rise to a dark-colored residue. It is this partial decomposition of the trisilicon octachloride that is responsible for the fact that the boiling point is not very sharp under atmospheric pressure. When the liquid is distilled, however, under diminished pressure, no decomposition occurs; the liquid can be repeatedly distilled under diminished pressure to the last drop, without any discoloured residue appearing in the flask. The boiling points were determined as follows:

Pressure.		Pressure.	
mm.	B. p.	mm.	B. p.
17	100°	74	137°
22	106	80	139
24	110	83	141
30	113	90	143
47	124	93	144
53	126.5	95	145
60	129	108	147
65	133	110	149
69	134.5	760	210-213
72	135.5		

The density was found to be  $D_4^{20}$  1.61, and the refractive index for sodium light ( $D$  line) 1.5135 at 14.5°. Gattermann and Weinlig (loc. cit.) gave the refractive index for "red light" as 1.52.

The liquid was analysed in the same way as disilicon hexachloride (p. 2853). (Found, Cl 76.99. Calc., Cl 76.97 per cent.)

#### *Isolation of Higher Chlorides.*

After separating the trisilicon octachloride as above described, etc. remained in the flask about 20 c.c. of a black liquid which boiled at above 220°. This was now subjected to fractional distillation under diminished pressure in a specially constructed small glass flask, fitted with a rod-and-disk fractionating column, the flask and fractionating column being fused together.

After very considerable difficulties, founded principally on the fact that the silicon chlorides must not be exposed to moist air, and the fact that only very small quantities were distilled, at least three distinct substances were separated after repeated distillation: (1) a viscous, colourless liquid (3 grams), boiling at about 150°/15 mm.; (2) a viscous, colourless liquid (2 grams), boiling at about 160°/15 mm.; and (3) a white, crystalline solid (0.5 gram), which melted at about 218°, and distilled at about 210°/12 mm. It was soluble in dry benzene or light petroleum, and could be crystallised therefrom. The examination of these substances is being continued.

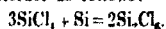
These chlorides, when thrown into water, yield white, amorphous products, easily combustible, which are no doubt the higher analogues of silico-oxalic and mesoxalic acid. These white substances also dissolve in potassium hydroxide to a clear solution with the evolution of hydrogen.

The examination of these products is being continued.

There remained in the flask at least 13 grams of a black, viscous mass, like tar or pitch, which was soluble in ether, insoluble in absolute alcohol, and evolved hydrogen with sodium hydroxide. The latter product, however, is still undergoing examination.

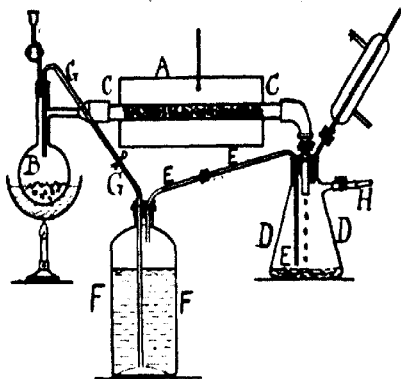
*Distillation of Silicon Tetrachloride over Silicon.*

According to Gattermann and Weinlig (*loc. cit.*), silicon and silicon tetrachloride interact as follows:



In order to test this the following apparatus was employed:

FIG. 3



By means of air pressure (from an air-pump) applied to the Winchester bottle *F*, pure silicon tetrachloride contained therein can be forced into the weighed flask *B*, which is heated on the water-bath. This silicon tetrachloride was then distilled from the flask *B* through an iron pipe *C* packed with commercial silicon broken into a coarse powder and heated in a Gattermann's bomb furnace *A*. The iron tube was about 120 cm. long and 3.1 cm. in internal diameter, with screwed-on iron terminal caps and connecting pieces, the screw-threads being made gas-tight by asbestos packing. The silicon tetrachloride passing through the tube *C* is condensed in the two-litre filter flask *D*. By means of an air-pump attached to the silicon tetrachloride accumulated in *D* could (after closing certain clips connected with the exit tubes from the apparatus) be forced back up the tube *EEE* into the reservoir *F*, and thence, if required, up the tube *GG* back into the flask *B*, so that the silicon tetrachloride in *F* could be repeatedly distilled over the silicon in *C* as many times as desired.

By means of this apparatus 3 kilos. of silicon tetrachloride free from disilicon hexachloride were repeatedly distilled over silicon

in the tube C, first of all when the latter was maintained at 200°, then at 280°, then at 310°, and lastly at 340°.

However, in no case were noticeable amounts of disilicon hexachloride found to have been formed in the distilled silicon tetrachloride.

Hence it is proved that the 20 per cent. yield of disilicon hexachloride stated by Gattermann and Weinlig to have been produced by the action of chlorine on silicon at 300–310° could not possibly have arisen, as they supposed, from the action of silicon tetrachloride on silicon.

*Distillation of Silicon Tetrachloride over Ferrosilicon.*

The preceding experiment was repeated, the silicon in the tube being now replaced by 50 per cent. ferrosilicon. However, in this case, also, no noticeable amounts of disilicon hexachloride could be proved to be produced when 3 kilos. of silicon tetrachloride were distilled over the mass, even when the tubes were heated to 300° and 340°.

It was thought that although ordinary silicon tetrachloride when distilled over ferrosilicon will not give rise to disilicon hexachloride, nevertheless it might be possible that silicon tetrachloride at its moment of formation might react with ferrosilicon to produce some disilicon hexachloride.

The easiest way to test this was to pass chlorine over a very long length of ferrosilicon, so that the silicon tetrachloride produced in the first part of the tube would then react with more ferrosilicon as it passed in the vaporous condition down the tube. Consequently, the following experiment was carried out:

A piece of Jena combustion tube, about 200 cm. long and 2 cm. bore, was drawn out at one end and bent at right angles. It was filled with a long layer of 50 per cent. ferrosilicon in the form of a coarse powder, and the tube was placed through two bomb furnaces in succession, and was therein heated to 300–310°, while a slow current of dry chlorine was passed through the tube. The resulting silicon tetrachloride was received in a distilling flask immersed in cold water.

It was found that when the action commenced, the chlorine was practically completely absorbed by the first 15 or 17 cm. of heated ferrosilicon, so that the silicon tetrachloride would have every opportunity as it passed over the succeeding lengths of ferrosilicon to react with more silicon to produce disilicon hexachloride. However, the resulting silicon tetrachloride was found on distillation to contain less than 4 per cent. of disilicon hexachloride. Since the average yield of disilicon hexachloride produced by passing

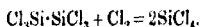


chlorine over short lengths of ferrosilicon considerably exceeded, and it is quite certain that the effect of passing silicon tetrachloride over a long length of heated ferrosilicon is not to increase the yield of disilicon hexachloride. If anything, it led to a diminution of the yield.

These experiments prove conclusively that the Gattermann-Weinlig reaction certainly does not proceed to a noticeable extent at low temperatures, and that therefore their explanation of the presence of disilicon hexachloride and higher chlorides in the silicon tetrachloride produced by chlorinating silicon or ferrosilicon is inadmissible.

#### *Action of Chlorine on Disilicon Hexachloride.*

The author's theory that complicated chlorinated silicon compounds are first produced when chlorine acts on silicon or metallic silicides, and that silicon tetrachloride is formed from these by the further action of chlorine, was now put to the test of experiment and it was definitely proved that chlorine acts vigorously on disilicon tetrachloride (and no doubt still more vigorously on the more unstable higher chlorides) at 300–340° so as to break up the chain of directly united silicon atoms, with the production of silicon tetrachloride, thus:



It was proved that disilicon hexachloride burns directly to silicon tetrachloride in the presence of chlorine, the experiment being carried out as follows:

A stream of chlorine (dried by passing through concentrated sulphuric acid) was passed into a 150 c.c. flask containing about 50 grams of pure disilicon hexachloride and heated on an oil-bath, the temperature of which was gradually raised to 165° or 170°. The leading tube of the distilling flask was inserted firmly through a cork at one end of an iron tube, whilst at the other end of the iron tube there was an iron elbow joint screwed on, which was fitted with a reducer. A piece of iron piping from this projected into a receiving flask, passing in through a rubber stopper. The receiving flask had its leading tube projecting into a similar flask, the two latter flasks being immersed in ice.

The iron tube was contained in a Gattermann's bomb furnace, the temperature of which was maintained at about 340°.

A continuous stream of chlorine was now passed through the apparatus. So long as the temperature of the oil-bath in which the first flask was immersed was not sufficiently high to cause the disilicon hexachloride to boil, the silicon tetrachloride was not

passed to be passing over rapidly into the receiving flask. Also, if the iron tube was kept at about  $120^{\circ}$ – $130^{\circ}$  and the disilicon hexachloride was allowed to distil through it in a stream of chlorine, no inflammation followed. If, however, the temperature of the tube was kept at  $300^{\circ}$ – $340^{\circ}$ , as soon as the vapour from the boiling disilicon hexachloride, mixed with chlorine, reached the iron tube a mild explosion took place, a red flame shot back into the flask, and the disilicon hexachloride could be observed burning with a reddish flame all over its surface in the atmosphere of chlorine.

When the supply of chlorine was checked the flame rose and burnt round the end of the tube projecting into the flask through which the chlorine entered, the chlorine here burning in an atmosphere of disilicon hexachloride vapour. Dense, brown fumes accompanied the combustion of the disilicon hexachloride, and at the same time the silicon tetrachloride produced as the result of the combustion streamed through the iron tube, and rapidly collected in the receiving flask, the liquid being of a dark colour.

The experiment, however, must be carried out with caution, or it may become dangerous. Although on one occasion about 40 grams of pure disilicon hexachloride were burnt to silicon tetrachloride in this manner with only a mild initial explosion, yet in another experiment a violent explosion suddenly occurred towards the end of the operation, the first flask being hurled with great violence into the air and shattered with a loud report.

The liquid which distilled over was proved to be almost entirely silicon tetrachloride, distilling almost to the last drop between  $50^{\circ}$  and  $70^{\circ}$ , and leaving an inappreciable weight of a brown film in the flask. Disilicon hexachloride boils at  $145^{\circ}$ , whereas silicon tetrachloride boils at  $59^{\circ}$ .

Although disilicon hexachloride will thus catch fire and burn in a stream of chlorine to silicon tetrachloride, yet it was proved that this action only took place at temperatures higher than the boiling point of the hexachloride. At the ordinary temperature disilicon hexachloride does not combine with chlorine to a noticeable extent.

This was proved as follows: Dry chlorine from a cylinder was passed first through a wash-bottle containing concentrated sulphuric acid, and then into a distilling flask containing about 270 grams of pure disilicon hexachloride, the chlorine escaping through another wash-bottle also containing concentrated sulphuric acid.

A very considerable amount of chlorine was observed to dissolve in the disilicon hexachloride in the flask, without, however, any visible signs of a chemical action taking place; thus no sensible evolution of heat could be detected as the chlorine entered the flask. The stream of chlorine was passed through the disilicon

hexachloride for about four hours, and the liquid containing dissolved chlorine was then allowed to remain for twenty-four hours.

When the liquid in the flask was heated (being connected for this purpose with a condenser and a receiver rendered moisture-proof by calcium chloride tubes), on the first application of heat the disilicon hexachloride appeared to boil at quite a low temperature. This effect, however, was entirely due to the escape of the dissolved chlorine, and on distilling the 270 grams of disilicon hexachloride certainly less than 1 c.c. of liquid passed over below 100°C., conclusively proving that no appreciable amount of silicon tetrachloride (b. p. 59°C.) was produced by the prolonged action of chlorine on disilicon hexachloride.

This experiment also proved the very great solubility of chlorine in disilicon hexachloride, a fact which does not appear to have been noted before.

The refractive indices of disilicon hexachloride and trichlorosilane octachloride were kindly determined for the author by Mr. H. J. Nettleton.

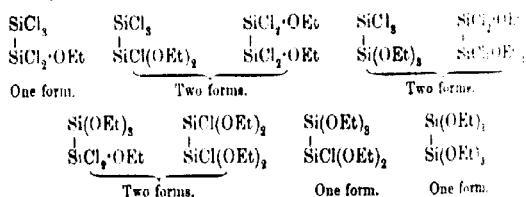
The author desires to thank the Senate of London University for a grant from the Dixon Fund which nearly covered the heavy expenses of the investigation. He also desires to thank the Chemical Society for likewise giving him a grant for the same purpose.

BIRKBECK COLLEGE,  
LONDON.

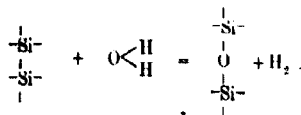
# CCLXVII.—*Researches on Silicon Compounds. Part VII. The Action of Ethyl Alcohol on Disilicon Hexachloride.*

By GEOFFREY MARTIN.

WHEN ethyl alcohol acts on disilicon hexachloride,  $\text{Si}_2\text{Cl}_6$ , the following nine substances are, theoretically, capable of being produced, none of which has hitherto been described:



The production of these substances has also considerable theoretical importance, because the chlorine atoms contained therein can be easily replaced by hydroxy groups merely by treatment with water, and the properties of the resulting hydroxy-compounds have some interest, as they afford means of verifying the author's theory\* (*Ber.*, 1912, **45**, 2097; 1913, **46**, 3289) that directly united silicon atoms, in the presence of attached oxygen atoms, are decomposed by alkalis with the evolution of hydrogen, according to the scheme:



Thus each direct Si-Si linking corresponds with the evolution of one molecule of evolved hydrogen. The properties and description of these hydroxy-compounds are best left to a later paper. The present paper is confined to the preparation and properties of the above-mentioned chlorinated compounds.

Having prepared a considerable amount of pure disilicon hexachloride as a starting point, the author was able to prepare in a pure condition compounds of the following formulae:  $\text{Si}_2\text{Cl}_4(\text{OEt})_2$ ,  $\text{Si}_2\text{Cl}_3(\text{OEt})_3$ ,  $\text{Si}_2\text{Cl}_2(\text{OEt})_4$ , and  $\text{Si}_2(\text{OEt})_6$ .

It will be noticed that each of the substances  $\text{Si}_2\text{Cl}_4(\text{OEt})_2$ ,  $\text{Si}_2\text{Cl}_3(\text{OEt})_3$ , and  $\text{Si}_2\text{Cl}_2(\text{OEt})_4$  can, theoretically, exist in two structurally different forms. However, in actual practice the author up to the present was unable to find more than one modification of each of these forms. Either the two modifications of each variety boil at the same temperature, or, what is more likely, the action proceeds almost to completion in one direction only, the one modification being produced in overwhelming amount and the other in traces, so that it is difficult to isolate the two isomerides.

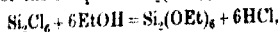
One curious fact that appears when alcohol is added to disilicon hexachloride is the circumstance that, apparently, a most vigorous action sets in, the mixture appearing to boil with the copious evolution of hydrogen chloride. Nevertheless, such an intense cold is produced that hoar-frost collects on the sides of the flask.

\* In view of Kipping's footnote (this vol., p. 484) I wish to draw attention to the note T, 1913, **103**, 119) in which I have dealt in detail with the accusations now created by him. With Kipping's suggestion that readers should refer to and compare the original papers bearing on the matter at issue I am in full agreement.

In regard to Kipping's statement that my preliminary note (*Ber.*, 1912, **45**, 2097) was published without his permission, I would point out that as the experiments were designed and carried out by myself alone, Kipping's permission was not necessary.

This is an example of a vigorous chemical action taking place with the absorption of so much heat that water can easily be frozen thereby.

The feebleness of the chemical forces tending to bring about the interchange of the chlorine atoms of the disilicon hexachloride for ethoxy-groups is also, no doubt, responsible for the fact that when disilicon hexachloride is treated with excess of alcohol, substitution of ethoxy-groups for chlorine does not proceed quantitatively and the production of the compound  $\text{Si}_2(\text{OEt})_6$ , thus:



but a mixture of lower chlorides is formed, and the last chlorine atoms of the disilicon hexachloride are quite difficult to displace by ethoxy-groups, repeated heating and distillation with excess of alcohol being necessary before the last traces of chlorine are expelled and the compound  $\text{Si}_2(\text{OEt})_6$  is obtained.

It is true that the first equivalents of chlorine of the disilicon hexachloride molecule are readily displaced by ethoxy-groups, but as each successive chlorine atom is removed the displacement proceeds with greater and greater difficulty, so that the substances  $\text{Si}_2\text{Cl}_4(\text{OEt})_2$  and  $\text{Si}_2\text{Cl}_2(\text{OEt})_4$  do not any longer fume very noticeably in air, and are scarcely acted on by ethyl alcohol at the ordinary temperature. They must be heated with alcohol to be, and above before any visible action, such as the evolution of hydrogen chloride, takes place.

The separation of these chlorinated silicon compounds by fractional distillation in a pure state proved a most difficult task, very prolonged and numerous fractionations being necessary before complete separation of the various components was effected. The difficulties were enormously increased by the fact that these substances react with traces of moisture, giving white, explosive precipitates, and causing a turbidity in the resulting liquids. Consequently, every vessel used in these repeated fractionations had to be most carefully freed from every trace of moisture by carefully washing out with alcohol, followed by ether, heating almost to redness in a luminous gas flame while a current of dry air was passed through the flask, and affixing fresh from the heating apparatus while still fairly hot to the fractionating apparatus. Only then can absolutely clear, colourless fluids, free from every trace of turbidity, be obtained. Moreover, in the fractionating apparatus corks had to be dispensed with as far as possible, and for this reason the long fractionating columns had to be fused on to the flask, the union by means of a cork proving unsatisfactory.

Rubber corks, after a time, were attacked by the liquids, becoming hard and cracked.

Other difficulties also arose, on account of the corrosive action of these liquids on the skin. They set up painful sores which took a long time to heal, and as in the repeated fractionations the changing of the vessels made contact of the fingers with these liquids almost unavoidable (owing to traces adhering to the sides, etc., of the vessels), it was found highly advisable to protect the thumb and fingers with indiarubber coverings.

In the following table are compared the physical properties of the different members of the series:

Substance.	Boiling point under 34 mm.	Density.	Refractive index (D line).
$\text{Si}_2\text{Cl}_6$	60.5	1.5624 <sup>25</sup>	1.4748 at 18
$\text{Si}_2\text{Cl}_5(\text{OEt})$	84	1.388 <sup>26</sup>	1.4568 „ 14.5
$\text{Si}_2\text{Cl}_4(\text{OEt})_2$	104	1.270 <sup>27</sup>	1.4432 „ 14.5
$\text{Si}_2\text{Cl}_3(\text{OEt})_3$	122	1.163 <sup>28</sup>	1.4333 „ 14.5
$\text{Si}_2\text{Cl}_2(\text{OEt})_4$	—	—	—
$\text{Si}_2\text{Cl}(\text{OEt})_5$	138	1.092 <sup>29</sup>	1.4205 „ 14.5
$\text{Si}_2(\text{OEt})_6$	141	0.9718 <sup>30</sup>	1.4134 „ 14.5

It will be seen that as we proceed down the series from  $\text{Si}_2\text{Cl}_6$  to  $\text{Si}_2(\text{OEt})_6$ , there is a progressive increase in the value of the boiling points; the substitution of a single chlorine atom in  $\text{Si}_2\text{Cl}_6$  by an ethoxy-group causes an increase in the boiling point of 23.5° 34 mm., but the successive displacements of chlorine by ethoxyl effects a rapidly diminishing value in the rise of the boiling point, until finally, the last two members of the series, namely,  $\text{Si}_2\text{Cl}(\text{OEt})_5$  and  $\text{Si}_2(\text{OEt})_6$ , boil at nearly the same temperature so near together, in fact, that it is difficult to separate a mixture of these two substances by fractional distillation.

The same gradation of physical properties is apparent when the densities are compared. Thus, whilst disilicon hexachloride has a density of 1.56, hexaethoxysilicoethane,  $\text{Si}_2(\text{OEt})_6$  (D 0.97), is actually lighter than water; the intermediate members of the series have intermediate values.

#### EXPERIMENTAL.

Some preliminary experiments were first made. In one case 5 grams of disilicon hexachloride were treated with about 100 c.c. of ethyl alcohol (99.8 per cent.), and in another case 21 grams of disilicon hexachloride were treated with 50 c.c. of ethyl alcohol.

In each case a vigorous action took place, much hydrogen chloride was evolved, and the liquid became so cold that the flasks containing the liquid became covered with ice, whilst a thermometer placed in one flask registered  $-9^\circ$ . Two layers of liquid were observed to form.

After distilling over the excess of alcohol the residual oils decom-

posed on distillation under the ordinary pressures, the thermometer rising rapidly to  $200^{\circ}$ , and dense brown fumes appeared in the flask and a brown mass remained behind.

Under diminished pressure, however, colourless oils distilled away without decomposition, but they were evidently mixtures, since under 15 mm. pressure some liquid distilled at  $65\text{--}96^{\circ}$ , but about 75 per cent. passed over at  $110\text{--}115^{\circ}/15$  mm., after which the thermometer rose and a small quantity of liquid distilled over at  $170\text{--}180^{\circ}/15$  mm.

Attempts to fractionate these liquids showed that they consisted of complex mixtures of different substances, and that when disilicon hexachloride is treated with excess of alcohol the action does not proceed quantitatively, thus:  $\text{Si}_2\text{Cl}_6 + 6\text{EtOH} = \text{Si}_2(\text{OEt})_6 + 6\text{HCl}$ , but leads to the production of intermediate chlorinated products in a very considerable quantity.

All these colourless oils contained chlorine, and when thrown into water they produced white precipitates, which dissolved on warming (but not in the cold) with sodium or potassium hydroxides with the evolution of hydrogen. They also evolved hydrogen with ammonia.

When thrown into water, however, the change from an oily to a white solid took some little time, and no heat perceptible to the hand (although perceptible to a thermometer) was evolved.

When exposed to the air in a dish the oils became transformed into transparent, solid glasses, which also possessed the power of dissolving in warm potassium hydroxide with the evolution of hydrogen.

That it was atmospheric moisture (and not oxygen) that converted the oils into glasses on exposure to air was proved by the fact that when equal quantities of the oils were exposed (1) to dry air in a desiccator (over sulphuric acid), and (2) to the ordinary moist air outside the desiccator, it was found that only the surface exposed to the moist air outside the desiccator exhibited this solidifying effect.

These preliminary experiments proved that the action of ethyl alcohol on disilicon hexachloride was no simple one, and that in order to isolate pure products considerable quantities of disilicon hexachloride would have to be treated with alcohol, and the resulting liquid very carefully fractionated.

Accordingly, in all, some 600 grams of disilicon hexachloride were treated with ethyl alcohol, and the products isolated after many months' fractional distillation, as described below.

*Pentachloroethoxysilico-ethane,  $\text{Si}_2\text{Cl}_5\text{OEt}$ , and Tetrachloro-diethoxysilico-ethane,  $\text{Si}_2\text{Cl}_4(\text{OEt})_2$ .*

Eighty-four grams of disilicon hexachloride (1 mol.) were placed in a flask fitted with a reflux condenser, and 15 grams (1.05 mol.) of ethyl alcohol were gradually run in (with continual shaking) through a stoppered funnel.

A vigorous action took place as the alcohol entered, much hydrogen chloride was evolved, and the liquid in the flask became slightly yellow and very cold, so that ice was deposited on the sides of the containing flask. A few drops of an orange-coloured liquid appeared to float on the surface of the liquid in the flask.

On heating, however, under a reflux condenser on the water-bath for one hour these orange-coloured drops gradually disappeared, the liquid finally appearing almost colourless. After leaving overnight the liquid was distilled under diminished pressure, using a Young's 15-rod-and-disk fractionating column fused on to the distilling flask.

However, a great many fractionations proved that the fractionating column used was not efficient enough to separate sharply the various components of the mixture, and it was also evident that larger quantities of material would have to be employed in order to obtain pure products. Four main fractions were isolated:

*Fraction 1.*—Up to  $80^\circ/35$  mm. The liquid boiled fairly constantly at  $60\text{--}65^\circ/35$  mm., then for some time at  $75^\circ/35$  mm. The thermometer rose slowly to  $80^\circ/35$  mm.

*Fraction 2.*— $80\text{--}90^\circ/35$  mm. The bulk passed over at  $82\text{--}87^\circ/35$  mm.

*Fraction 3.*— $90\text{--}100^\circ/35$  mm.

*Fraction 4.*— $100\text{--}110^\circ/35$  mm.

The experiment was repeated three times, using the following quantities: (1) 101 grams of disilicon hexachloride and 21 grams of ethyl alcohol. (2) 100 grams and 21 grams respectively. (3) 105 grams and 22 grams respectively. This makes in all about 390 grams of disilicon hexachloride treated with 79 grams of ethyl alcohol.

Each of these fractions was then fractionated, using a Young's 15-rod-and-disk fractionating column, with the result that there were finally obtained, after a very prolonged series of fractionations:

(1) A colourless, fuming liquid, boiling at  $50\text{--}52^\circ/35$  mm. and  $131\text{--}136^\circ/767$  mm., which contained silicon and chlorine, but was not disilicon hexachloride (which boils at  $145^\circ/760$  mm.). The yield was, however, only 8 c.c., and it was certainly not pure, so that it was not further examined.



(2) About 17 c.c. of a fuming, colourless liquid, boiling at  $59-61^{\circ}/35$  mm. and  $144-146^{\circ}/767$  mm., which was unchanged by distillation.

(3) One hundred grams of a colourless, mobile, fuming liquid, boiling at  $83.5-84.5^{\circ}/34$  mm., which was pentachloroethoxysilicoethane,  $\text{Si}_2\text{Cl}_5\cdot\text{OEt}$  (see below).

(4) Fifty-four grams of a colourless, fuming liquid, boiling at  $104^{\circ}/35$  mm., which proved to be tetrachlorodiethoxysilicoethane.

(5) About 155 grams of residues separated from the various fractionations in isolating the fractions (3) and (4).

Since both the liquids (3) and (4) boiled constantly, and all efforts to alter their boiling points proved unavailing, they were analysed as follows:

The liquid was introduced into a weighing bottle (without touching the sides, etc., of the latter) by means of a small pipette (fitted with a rubber teat, the stopper quickly inserted, and the weight weighed. Water was then quickly introduced into the weighing bottle in order to decompose the chloride. The white solid which appeared was first treated with concentrated ammonia which caused the evolution of hydrogen, and thus loosened the precipitate adhering to the sides of the vessel), and the liquid and precipitate were rinsed out into a beaker and warmed for some time on a water-bath with a little ammonia until the effervescence of hydrogen ceased. The liquid could be then either acidified with nitric acid and the chlorine estimated by the Volhard method, or exactly neutralised with nitric acid, and the chlorine estimated by titrating with  $N/10$  silver nitrate, using potassium chromate as indicator.

In the present case the clear liquid was filtered from the precipitate, the latter being well washed, and the liquid was neutralised with nitric acid, made up to 250 c.c., and titrated with  $N/10$  silver nitrate.

*Liquid (3) (b. p.  $83.5-84.5^{\circ}/35$  mm.):*

0.5910 gave  $\text{Cl} = 63.7$ .

$\text{C}_2\text{H}_5\text{OCl}_5\text{Si}_2$  requires  $\text{Cl} = 63.6$  per cent.

The liquid, therefore, was practically pure pentachloroethoxysilicoethane,  $\text{Si}_2\text{Cl}_5\cdot\text{OEt}$ .

*Liquid (4) (b. p.  $104^{\circ}/35$  mm.):*

0.8990 gave  $\text{Cl} = 49.7$ .

$\text{C}_4\text{H}_{10}\text{O}_2\text{Cl}_4\text{Si}_2$  requires  $\text{Cl} = 49.1$  per cent.

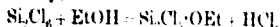
This liquid, therefore, needed some purification. It was treated with a very small amount of alcohol to remove the excess of chlorine, and the liquid was again fractionated, the first and last portions of the distillate being rejected. The liquid finally obtained, which boiled at the same temperature as that given above, was found to

contain Cl=49.2, and so was practically pure tetrachlorodiethoxy-silico-ethane,  $\text{Si}_2\text{Cl}_4(\text{OEt})_2$ .

*Pentachloroethoxysilico-ethane*,  $\text{Si}_2\text{Cl}_5\text{OEt}$ , is a mobile, colourless, fuming liquid, boiling at  $83.5\text{--}84.5^\circ/35$  mm., having  $D_4^{20}$  1.388 and  $n_D^{20}$  1.4568. It does not solidify when immersed in a freezing mixture of ice and salt. When exposed to moisture it is converted into a white solid, which can be made to explode by touching with a hot glass rod or even by brushing with a test tube brush. A full description of these explosive hydroxy-derivatives is reserved for a later paper.

*Tetrachlorodiethoxysilico-ethane*,  $\text{Si}_2\text{Cl}_4(\text{OEt})_2$ , is a mobile, colourless, fuming liquid, boiling at  $104^\circ/34$  mm., and having  $D_4^{20}$  1.270 and  $n_D^{20}$  1.4432. It does not freeze when immersed in a mixture of ice and salt. It is decomposed by water to form an explosive white hydroxy-compound.

The preceding results prove that in general when one equivalent of alcohol acts on disilicon hexachloride the reaction by no means proceeds quantitatively, thus:



Although pentachloroethoxysilico-ethane is the main product, a very considerable amount (more than 30 per cent.) of tetrachloroethoxysilico-ethane is produced at the same time, and the consequence is that some free disilicon hexachloride is left uncombined, and can actually be separated from the mixture by fractional distillation.

*Trichlorotriethoxysilico-ethane*,  $\text{Si}_2\text{Cl}_3(\text{OEt})_3$ .

From the previous distillations there had accumulated about 155 grams of residues, consisting mainly of a mixture of pentachloroethoxy- and tetrachlorodiethoxy-silico-ethane, together with some trichlorotriethoxysilico-ethane and similar products. In order to convert this mixture into the trichloro-derivative, 55 c.c. of ethyl alcohol (99.8 per cent.) were gradually added and the mixture constantly shaken, and heated on the water-bath for one hour. As the ethyl alcohol entered a vigorous action ensued, much hydrogen chloride was evolved, and the flask became very cold. After leaving overnight the liquid was fractionated under diminished pressure, using a Young's 20-rod-and-disk fractionating column fused on to the distilling flask.

Only a few c.c. passed over between  $60^\circ$  and  $115^\circ/35$  mm. At  $115\text{--}116^\circ/35$  mm. the thermometer remained constant until about 10–15 c.c. of liquid had distilled over. The bulk of the liquid passed over between  $123^\circ$  and  $125^\circ/35$  mm., about 80 c.c. being here collected, and the thermometer then rose to  $130\text{--}135^\circ/35$  mm.

On cooling, the residue in the flask solidified after standing over night, forming a dirty grey mass, which melted when gently heated.

The various fractions were now subjected to a prolonged and careful series of fractionations, whereby there was isolated about 50 grams of a liquid boiling constantly at 123—124°/35 mm.

0.5741 gave  $\text{Cl} = 35.6$ .

$\text{C}_6\text{H}_{15}\text{O}_3\text{Cl}_3\text{Si}_2$  requires  $\text{Cl} = 35.7$  per cent.

*Trichlorotriethoxysilico-ethane* is a colourless, fuming liquid, boiling at 123—124°/35 mm., and having  $D_4^{20}$  1.163 and  $n_D^{20}$  1.4333. It does not solidify when immersed in a freezing mixture of ice and salt. It is soon decomposed by atmospheric moisture, yielding a white, explosive hydroxy-compound. The liquid acts strongly on the skin, causing deep and painful wounds, which do not readily heal.

*Attempt to Isolate Dichlorotetraethoxysilico-ethane,  $\text{Si}_2\text{Cl}_2(\text{OEt})_4$*

From the previous distillations there had accumulated about 111 grams of liquid, largely consisting of trichlorotriethoxysilico-ethane, together with some tetrachlorodiethoxy- and dichloropentaethoxy-silico-ethane. This mixture was placed in a flask, and about 60 c.c. of ethyl alcohol were run in with constant shaking. Much hydrogen chloride was evolved, and the liquid became very turbid. The mixture was then subjected to fractional distillation. Nearly all passed over between 130° and 137°/33 mm., the bulk distilling at 131—132°/33 mm.

After prolonged fractionation a colourless liquid was isolated, boiling at 132—133°/35 mm., 121°/23 mm., 116°/18 mm., and 110°/12 mm.

Nearly 70 grams of this liquid were isolated, and this was shown by analysis (Found,  $\text{Cl} = 17.3$ ) to be a mixture of dichlorotetraethoxy- ( $\text{Cl} = 23.0$ ) and chloropentaethoxy-silico-ethane ( $\text{Cl} = 11.1$ ).

The mixture was subjected to prolonged fractional distillation, whereby some of the first fractions had their chlorine content raised to 18.7 per cent. However, it was not found possible to obtain dichlorotetraethoxysilico-ethane,  $\text{Si}_2\text{Cl}_2(\text{OEt})_4$ , in a pure condition, the boiling points of the mono- and di-chloro-derivatives being so close together as to make a complete separation of both by fractional distillation alone a matter of considerable difficulty, at least with the small quantities available.

*Chloropentaethoxysilico-ethane,  $\text{Si}_2\text{Cl}(\text{OEt})_5$*

With the object of isolating the above compound, some of the residues and fractions from previous distillations, amounting to—

about 66 grams, were collected and placed in a flask, and about 3 grams of ethyl alcohol were added. On adding the alcohol, however, apparently no action took place at the ordinary temperature, the liquid becoming neither sensibly hot nor cold to the hand, nor was any visible amount of hydrogen chloride evolved. On heating, however, an action set in, some hydrogen chloride being evolved.

It is thus evident that as the substitution of the chlorine for ethoxy groups in the disilicon hexachloride molecule proceeds, the action takes place less and less readily, substances like dichlorotetraethoxysilico-ethane not being noticeably acted on by alcohol at the ordinary temperature, although this action takes place readily enough on heating.

During the distillation, however, the flask, while being heated on a metal bath, burst, and the liquid was lost.

A fresh attempt was therefore made to isolate chloropentaethoxydisilico-ethane by acting on disilicon hexachloride with the theoretical amount of alcohol.

Disilicon hexachloride (138 grams; 1 mol.) was placed in a flask and treated with 99.8 ethyl alcohol (120 grams). Hydrogen chloride was evolved, and the flask became cold. The liquid, after being heated on the water-bath to complete the action, was fractionally distilled under diminished pressure, the heating being carried out on a metal bath. After about 80 grams of a liquid boiling at  $120-124^{\circ}$ , 15 mm. had distilled over, and while the flask was nearly half full of residual liquid, a violent explosion took place, the flask being shattered, and the fragments hurled vertically into the air with such force that an indentation was made in the hard plaster on the ceiling, 4 or 5 metres above the working bench.

The employment of a metal bath, therefore, for heating the flask appeared inadvisable, as the explosion possibly arose from overheating the residues of high boiling point left in the flask. As will be shown in a subsequent paper, many compounds containing silicon atoms directly united are explosive under certain conditions.

In all the subsequent distillations the flasks were heated on oil-baths, the temperatures of which were carefully controlled so as to avoid overheating, and with this precaution no further explosions were met with in the course of many subsequent distillations.

The preceding experiment was once more repeated, with precautions against overheating. Disilicon hexachloride (138 grams) was placed in a flask, and 99.8 per cent. ethyl alcohol (120 grams) was gradually added. Hydrogen chloride was evolved, and cold was produced. The liquid was then heated on the water-bath for one

hour until the evolution of hydrogen chloride had ceased, and the flask and its contents were allowed to remain overnight.

The weight of the contents of the flask after the evolution of hydrogen chloride had ceased was 167 grams, so that 138 grams of disilicon hexachloride had yielded about 167 grams of product and lost 91 grams of hydrogen chloride.

According to the equation  $\text{Si}_2\text{Cl}_6 + 5\text{EtOH} = \text{Si}_2\text{Cl}(\text{OEt})_5 + \text{H}_2$ , 138 grams of disilicon hexachloride should give 161 grams chloropentaethoxysilico-ethane and lose 93 grams of hydrogen chloride.

The numbers actually found agree sufficiently closely with the theoretical to make certain that the action had taken place almost quantitatively.

The liquid was therefore fractionally distilled, the fractionating flask being immersed in an oil-bath, the temperature of which was not allowed to rise above  $175^\circ$  in order to avoid the danger of overheating.

After about 20 grams of liquid had passed over between  $120^\circ$  and  $120^\circ/15$  mm., the main fraction of 112 grams passed over boiling very constantly, between  $120^\circ$  and  $123^\circ/15$  mm. In the flask remained about 25 grams of residue of higher boiling point. The main fraction, boiling at  $120^\circ\text{--}123^\circ/15$  mm., was now subjected to fractional distillation, using a Young's 20 rod and net column fused on to the distilling flask, which was heated in an oil-bath to about  $160^\circ$ . There was thus obtained a fraction boiling very constantly at about  $121^\circ/15$  mm.

However, the substance was certainly not quite pure, a chlorine determination, carried out as previously described, using chromous as indicator, giving  $\text{Cl}=12.0$  (Calc.,  $\text{Cl}=11.2$  per cent). Consequently, the excess of chlorine was removed by adding a very little alcohol to the liquid, and then subjecting it to fractional and repeated distillation, neglecting the first and last parts of the distillate.

There was thus obtained the main bulk of liquid, which, when three successive fractions were taken, all boiled at the same temperature of  $126^\circ\text{--}127^\circ/19$  mm., and seemed quite pure.

A chlorine estimation was next carried out with each of the three successive fractions, and gave, respectively,  $\text{Cl}=11.3$ ,  $\text{Cl}=11.2$ ,  $\text{Cl}=11.1$ .

There is no doubt, therefore, that the substance was fairly pure chloropentaethoxysilico-ethane, which requires  $\text{Cl}=11.2$  per cent.

*Chloropentaethoxysilico-ethane*,  $\text{Si}_2\text{Cl}(\text{OEt})_5$ , is a colorless liquid ( $D_4^{20}$  1.092,  $n_D^{20}$  1.4205) which does not fume noticeably in the air, but on exposure to atmospheric moisture gives a white

amorphous, explosive hydroxy-compound. The liquid does not solidify when immersed in a freezing mixture of ice and salt. The boiling points were determined under different pressures, as follows:

Pressure .....	13 mm.	14 mm.	15 mm.	16 mm.	18 mm.	20 mm.	22 mm.
Boiling point .....	119°	120°	121°	122°	124°	127°	129°
Pressure .....	23 mm.	24 mm.	27 mm.	30 mm.	32 mm.	36 mm.	
Boiling point .....	130°	131°	134°	136°	137°	139°	

### Hexaethoxysilico-ethane, $\text{Si}_2(\text{OEt})_6$

About 151 grams of chloropentaethoxysilico-ethane, prepared as previously described, and boiling at about 120°–121°/15 mm., was placed in a flask fitted with a reflux condenser. On adding about 10 c.c. of ethyl alcohol (1 mol.), no visible action appeared to take place. On heating on the oil-bath, however, the evolution of hydrogen chloride began at about 100°, and became quite vigorous when the temperature of the oil-bath reached 110°–120°, showing that the action,  $\text{Si}_2\text{Cl}(\text{OEt})_5 + \text{EtOH} = \text{Si}_2(\text{OEt})_6 + \text{HCl}$ , was proceeding.

On distilling the liquid, which passed over for the most part between 120° and 124°/15 mm., no alcohol distilled over, so that the absorption of alcohol was complete. However, a little chlorine was present in the distillate, and in order to remove this about 20 c.c. of alcohol were added, and the liquid was heated on the water-bath under a reflux condenser. The excess of alcohol could be distinctly seen distilling up the condenser, condensing, and dropping back on the liquid in the flask, so that excess of alcohol was certainly present.

The alcohol was distilled over, and in it was found a perceptible amount of chlorine. The liquid was therefore repeatedly boiled with alcohol, the excess of alcohol being distilled off each time. It was found very difficult, even when excess of alcohol was repeatedly present, to expel every trace of chlorine, proving that the above reaction by no means readily proceeds to completion.

However, there was finally obtained a colourless, non-fuming liquid boiling at 123°/15 mm., which, after repeated fractionation with a Young 20-rod-and-disk fractionating column fused on to the distilling flask, was found to be free from chlorine. In analysing the liquid, the silicon was estimated by heating some of the substance in a platinum crucible with concentrated sulphuric acid, igniting, and weighing the resulting silica:

0.2800 gave 0.4499  $\text{CO}_2$  and 0.2354  $\text{H}_2\text{O}$ . C=43.8; H=9.4; Si=17.2.

1.1281 gave 0.4120  $\text{SiO}_2$ .

$\text{C}_{12}\text{H}_{20}\text{O}_6\text{Si}_2$  requires C=44.07; H=9.2; Si=17.3 per cent.

*Hexaethoxysilico-ethane* is a colourless, non-fuming liquid which does not solidify in a freezing mixture of ice and salt. It boils at 123°/15 mm., 132°/24 mm., 137.5°/30 mm., and 141°/34 mm. and has  $D_4^{20}$  0.9718 and  $n_D^{20}$  1.4134. The boiling points are very close to those of chloropentaethoxysilico-ethane. It is decomposed by alkali, with the evolution of hydrogen.

The refractive indices recorded in this paper were kindly determined by Mr. H. R. Nettleton, at the author's request.

The author desires to express his thanks to the Research Committee of the Chemical Society for a grant which defrayed a small part of the cost of this investigation; also to the Senate of London University for a grant from the Dixon Fund which defrayed the main part of the expenses.

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### CCLXVIII.—*The Isomerism of the Oximes. Part V* *p*-Dimethylaminobenzaldoxime.

By OSCAR LITTLE BRADY and FREDERICK PERCY DUNN

ALTHOUGH *p*-dimethylaminobenzaldoxime,  $\text{NMe}_2\text{C}_6\text{H}_4\text{CH=N-OH}$  has been described (Knofler and Boessneck, *Ber.*, 1887, 20, 316) it has not been studied from the point of view of the Harlow-Werner hypothesis.

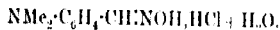
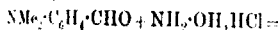
As this compound contains no possibly labile hydrogen atom, the para-substituting group it would be expected to exist in two isomeric forms, *anti* and *syn* (compare Brady and Dunn, *loc. cit.* vol., p. 824); indeed, as the basicity of the substituting group seems to influence the stability of the two isomerides, it is possible that the oxime prepared from *p*-dimethylaminobenzaldehyde by the usual methods would be a *syn*-derivative, or, if not, the *syn*-isomeride would be readily obtained from it, and would be more stable than is usually the case with these compounds. Additional interest is added by the fact that no benzaldoxime containing a basic group as a substituent has been obtained in two isomeric forms; indeed, compounds of this class have been little studied.

As regards the preparation of a *syn*-derivative of this compound the authors' expectations have not been fulfilled, and *p*-dimethyl-

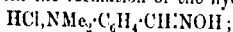
benzalaldehyde oxime must be added to the considerable number of aromatic aldoximes that appear to exist only in one form.

The oxime as ordinarily prepared by the action of hydroxylamine hydrochloride on the aldehyde in the presence of sodium carbonate has undoubtedly the *anti*-configuration, since it yields an acetyl derivative and not a nitrile on treatment with acetic anhydride and sodium carbonate solution. This acetyl derivative yields the original oxime on hydrolysis with alkalis. Dry hydrogen chloride, when passed into a dry ether or chloroform solution of the oxime, precipitates a hydrochloride which regenerates the original oxime on treatment with sodium carbonate solution. Under the above conditions the oxime unites with only one molecule of hydrogen chloride, and it was possible that the acid was attached to the dimethylamino- and not to the oximino-group, a fact which would account for the failure to obtain a *syn*-oxime. Support is lent to this contingency by the behaviour of the *O*-methyl ether of *p*-dimethylaminobenzaldehyde oxime, which readily yields a hydrochloride under similar conditions, differing in this respect from the *O*-methyl ethers of oximes which contain no basic substituent in the benzene ring. On the other hand it is noteworthy that the hydrochloride of the *O*-methyl ether, in which the hydrogen chloride is undoubtedly attached to the dimethylamino-group, does not evolve hydrogen chloride at its melting point, whereas the hydrochloride obtained from *p*-dimethylaminobenzaldehyde oxime resembles the hydrochlorides of other oximes and suffers decomposition at its melting point owing to loss of hydrogen chloride.

An attempt was made to overcome this difficulty by preparing the hydrochloride directly from the aldehyde and hydroxylamine hydrochloride in the absence of alkali (Beckmann, *Annalen*, 1909, 365, 201):



This method yielded, however, a hydrochloride melting at the same temperature as the hydrochloride obtained from the oxime, and this hydrochloride gave the *anti*-oxime on treatment with sodium carbonate solution. It is possible that by this method the hydrochloride,  $\text{NMe}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}:\text{NOH}, \text{HCl}$ , is first formed which is then decomposed with the formation of the hydrochloride,

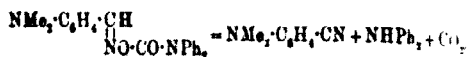


this seems, however, unlikely, although the basic nature of the amino-group is much less marked than that of the dimethylamino-group.

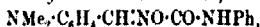
Diphenylcarbamyl-*p*-dimethylaminobenzaldehyde oxime has been prepared, and like other diphenylcarbamyl derivatives of the aromatic



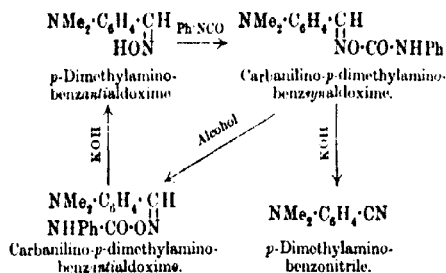
aldoximes has the *syn*-configuration, yielding on hydrolysis diphenylamine and *p*-dimethylaminobenzonitrile (compare Brady and Dunn, T., 1913, 103, 1613):



*Carbanilino-p-dimethylaminobenzaldoxime*,



obtained by the action of phenylcarbimide on the oxime, is of especial interest as it resembles carbanilino-*m*-nitrobenzaldoxime in that the compound first obtained, on boiling with alcohol, changes to an isomeric compound of higher melting point, which seems still to be a carbanilino-oxime. Up to the present there has been no satisfactory explanation suggested for the existence of the three carbanilino-derivatives obtained from the *m*-nitrobenzaldoxime, two from the *anti*- and one from the *syn*-compound. The authors have been engaged for some time on this question, which will form the subject of their next communication; for the present it will be sufficient to state that the carbanilino-derivative of *p*-dimethylaminobenzaldoxime as prepared by the action of phenylcarbimide on the *anti*-oxime is the *syn*-derivative, and gives on hydrolysis *p*-dimethylaminobenzonitrile and aniline, whereas the product of higher melting point obtained by boiling this compound with alcohol is the *anti*-compound, and on hydrolysis gives aniline and *p*-dimethylaminobenzaldoxime as its main decomposition products.



#### EXPERIMENTAL.

The *p*-dimethylaminobenzaldoxime employed was prepared by Knofer and Boessneck's method (*loc. cit.*) by boiling a mixture of the aldehyde, hydroxylamine hydrochloride, and anhydrous sodium carbonate in equivalent proportions with alcohol under a reflux condenser for three hours, and pouring the product into water. As, however, in the authors' experiments the oxime separated as a

crystalline solid on stirring the aqueous emulsion, it was removed by filtration instead of extraction with ether. After recrystallisation from alcohol the oxime melted at  $144^{\circ}$ .

*Acetyl-p-dimethylaminobenzantialdoxime.*—The oxime was dissolved in acetic anhydride, warming very gently, and left for fifteen minutes. A bright green solution was thus obtained (it may be noted here that this colour is very generally met with in working with dimethylaminobenzaldoxime, and is probably due to a trace of some oxidation product). The excess of acetic anhydride was decomposed by shaking with sodium carbonate solution, when the acetyl derivative was obtained as a mass of pale green crystals, which separate from dilute alcohol in colourless needles melting at  $108^{\circ}$ .

0.1569 gave 18.2 c.c.  $N_2$  at  $11^{\circ}$  and 746 mm.  $N = 13.7$ .

$C_{11}H_{14}O_2N_2$  requires  $N = 13.6$  per cent.

This compound was boiled for ten minutes with 2*N*-sodium hydroxide when it passed completely into solution, the solution was acidified with dilute sulphuric acid, and made faintly alkaline with sodium carbonate; the solid separating proved to be *p*-dimethylaminobenzaldoxime, and acetic acid could be detected in the mother liquor. The formation of this acetyl derivative and its hydrolysis establish the *anti*-configuration of the oxime.

#### *Action of Hydrogen Chloride on p-Dimethylaminobenzantialdoxime.*

The oxime was dissolved in anhydrous ether, and dry hydrogen chloride passed into the solution; a yellow, pasty mass was first precipitated, which rapidly became white and crystalline. The hydrochloride obtained in this way melted and decomposed at  $170^{\circ}$ :

0.3078 required 15.2 c.c.  $N/10$ - $AgNO_3$ .  $Cl = 17.5$ .

$C_9H_{12}ON_2.HCl$  requires  $Cl = 17.7$  per cent.

When decomposed with sodium carbonate solution the original oxime was obtained, the crude product melting at  $140^{\circ}$ , and after recrystallisation from cold acetone and water at  $144^{\circ}$ , moreover, admixture with this substance did not depress the melting point of *p*-dimethylaminobenzantialdoxime.

The action of dry hydrogen chloride on a solution of the oxime in dry chloroform was also investigated, but a hydrochloride of the same melting point was obtained, and this also regenerated the original oxime on treatment with sodium carbonate solution. The hydrochloride was also prepared according to Beckmann's method (*loc. cit.*). Equivalent quantities of the aldehyde and hydroxylamine hydrochloride were heated in alcohol for three hours at

50--55°. A copious precipitate formed, which proved to be the same hydrochloride as previously obtained, melting at 170° and giving *p*-dimethylaminobenzantaldoxime on treatment with sodium carbonate solution.

*O*-Methyl Ether of *p*-Dimethylaminobenzantaldoxime. This was prepared in the usual way by boiling on the water-bath for three minutes an alcoholic solution of the oxime with an equivalent amount of sodium ethoxide and a slight excess of methyl ether. The green product was poured into water and extracted with ether, the ethereal solution being shaken with sodium hydroxide solution to remove unaltered oxime, washed with water, and evaporated. A pale amber-coloured oil was thus obtained, which when cooled on ice set to a greenish-white, crystalline mass. On recrystallising from dilute alcohol the ether separates in colourless plates with a slight fragrant odour, and melting at 69°:

0.1638 gave 32.2 c.c.  $N_2$  at 17° and 751 mm.  $N = 15.8$ .

$C_{10}H_{14}ON_2$  requires  $N = 15.7$  per cent.

*Hydrochloride of the O-Methyl Ether of p-Dimethylaminobenzantaldoxime.*

The *O* methyl ether was dissolved in dry ether, and dry hydrogen chloride was passed into the solution. A viscid substance was precipitated, which soon became crystalline. This hydrochloride melts at 118--122°, but, unlike the hydrochlorides of the oxime, does not evolve hydrogen chloride at its melting point:

0.2134 required 10.0 c.c.  $N/10$ -AgNO<sub>3</sub>.  $Cl = 16.6$ .

$C_{10}H_{14}ON_2 \cdot HCl$  requires  $Cl = 16.5$  per cent.

Decomposition of the hydrochloride with sodium carbonate solution regenerated the *O* methyl ether.

*Diphenylcarbamyl-p-dimethylaminobenzsynaldoxime.*

This compound was prepared by dissolving the oxime in alcohol and adding one equivalent of sodium in alcohol and one equivalent of diphenylcarbamyl chloride. On adding the latter a voluminous, pasty mass was formed, which was well shaken, heated on the water-bath for ten minutes, cooled, filtered, and washed with water. This substance is almost insoluble in hot alcohol, but is readily soluble in chloroform, and may be recrystallised from a mixture of this solvent and light petroleum, when it separates as small, colourless needles, melting and decomposing at 171°:

0.2930 gave 29.0 c.c.  $N_2$  at 16° and 751 mm.  $N = 11.5$ .

$C_{22}H_{21}O_2N_3$  requires  $N = 11.7$  per cent.

Diphenylcarbamyl-*p*-dimethylaminobenzsynaldoxime was hydro-

used by boiling with alcoholic sodium hydroxide for two hours. The sodium carbonate which separated was filtered off, and the solution diluted considerably with water and filtered. The solid obtained was washed repeatedly with very dilute hydrochloric acid, and the residue recrystallised from alcohol; this proved to be diphenylamine. The washings were extracted with ether to remove diphenylamine, then made alkaline, and again extracted with ether. After removal of the ether the residue was crystallised from alcohol, and found to be dimethylaminobenzonitrile. From the first filtrate there was a small quantity of dimethylaminobenzaldoxime was obtained by extracting the alkaline solution with ether to remove diphenylamine, etc., acidifying, making faintly alkaline with sodium carbonate, and again extracting with ether. This ethereal solution yielded a small quantity of solid, which was recrystallised from alcohol and shown to be the oxime.

*Carbanilino-p-dimethylaminobenzaldoxime*.—A solution of dimethylaminobenzaldoxime in ether was treated with an equimolecular amount of phenylcarbimide. After a few moments the brown, shining plates began to separate; the solution was left for twenty-four hours and then filtered. The solid was recrystallised from cold acetone and water, from which solution it separated as sulphur-yellow plates, melting and decomposing at  $117^{\circ}$ . A further recrystallisation from alcohol removed most of the colour, but did not raise the melting point:

0.2021 gave 25.2 c.c.  $N_2$  at  $16^{\circ}$  and 761 mm. N = 14.7.

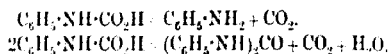
$C_{16}H_{17}O_2N_3$  requires N = 14.8 per cent.

This carbanilino-derivative was hydrolysed by boiling with ten per cent. sodium hydroxide solution for five minutes. Aniline was easily recognised in the steam, whilst oily drops remained suspended in the liquid. These on cooling set to a solid, which was recrystallised from dilute alcohol, and melted at  $75^{\circ}$ ; a mixture with *p*-dimethylaminobenzaldehyde (m. p.  $73^{\circ}$ ) melted at  $55^{\circ}$ , and with *p*-dimethylaminobenzonitrile (m. p.  $75-76^{\circ}$ ) at  $75^{\circ}$ . The mother liquor from the hydrolysis was acidified, and then made faintly alkaline with sodium carbonate solution, when, after some time, a small quantity of substance crystallised out, which proved to be *p*-dimethylaminobenzaldoxime, formed probably by the conversion of a little of the *syn*- into the *anti*-carbanilino compound during the warming and the subsequent hydrolysis of the latter.

A similar decomposition takes place if the carbanilino-derivative is heated with alcohol alone for some time. Carbanilino-*p*-dimethylaminobenzaldoxime was boiled with alcohol under a reflux condenser for twenty-four hours; the solution so obtained was diluted with about half its volume of water and cooled. The crystalline

precipitate which formed proved to be diphenylcarbamide (m.p. 232°). The mother liquor was diluted, and the milky liquid acidified with dilute hydrochloric acid; silky needles which remained suspended in the solution were collected, and shown to be diphenylcarbamide. The filtrate was again made alkaline with sodium hydroxide, stirred, and set aside for some hours, when a quantity of dimethylaminobenzonitrile separated out. The mother liquor was acidified and made alkaline with sodium carbonate, and the solid separating was crystallised from alcohol, and proved to be dimethylaminobenzaldoxime.

In each of the above cases the primary products of the reaction may be regarded as *p*-dimethylaminobenzonitrile and the hypothetical phenylcarbamic acid; the latter in the presence of alkali is decomposed into carbon dioxide and aniline, and in the absence of alkalis two molecules yield water, carbon dioxide, and diphenylcarbamide:



The much larger amount of oxime found as the result of prolonged boiling with alcohol is due to the conversion of most of the *syn*- into the *anti*-derivative, and the subsequent hydrolysis of the compound (see below).

*Carbanilino-p*-dimethylaminobenzaldoxime. The itridly prepared *syn*-carbanilino-derivative described above was covered with alcohol and boiled under a reflux condenser for one hour. On cooling, carbanilino-*p*-dimethylaminobenzaldoxime crystallised in large, colourless plates, melting and decomposing at 152°.

0.2646 gave 32.4 c.c.  $\text{N}_2$  at 13° and 768 mm.  $\text{N} = 14.9$ .

$\text{C}_{16}\text{H}_{17}\text{O}_2\text{N}_3$  requires  $\text{N} = 14.8$  per cent.

This compound is also formed if the *syn*-carbanilino-derivative is kept for any length of time, there being formed simultaneously a small amount of aniline and dimethylaminobenzonitrile. Carbanilino-*p*-dimethylaminobenzaldoxime on boiling with 2*N* sodium hydroxide passes almost completely into solution, no nitrile being formed; the solution on treatment in the usual way yields dimethylaminobenzaldoxime and aniline.

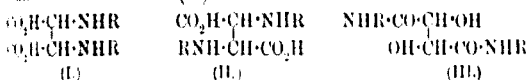
In conclusion, the authors beg to express their thanks to the Research Fund Committee of the Chemical Society for a grant which has defrayed the expenses of this work.

ROYAL COLLEGE OF SCIENCE,  
THE IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,  
SOUTH KENSINGTON.

CXLIX.—*The Reaction Between Benzylamine and the Dibromosuccinic Acids.*

By EDWARD PERCY FRANKLAND.

It has been shown by the author (T., 1911, **99**, 1775) that *meso*-dibromosuccinic acid\* and benzylamine react to form a dibenzylaminosuccinic acid and, simultaneously, the dibenzylamide of tartaric acid. Analogous results have now been obtained with *r*-dibromosuccinic acid,\* which yields an isomeric dibenzylaminosuccinic acid, together with a small quantity of the dibenzylamide of racemic acid. A comparison of the properties of the two dibenzylamino-acids suggests that the one obtained from *meso*-dibromosuccinic acid has a structure corresponding with that of tartaric acid, and resembles the diaminosuccinic acid prepared by Lehrfeld from *meso*-dibromosuccinic acid, which Tafel has shown to yield tartaric acid when treated with nitrous acid. On the assumption that the configurations of the groups about the two asymmetric carbon atoms are similarly affected by the reagent (nitrous acid), the configuration of the diamino acid will be the same as that of the tartaric acid derived from it. Consequently, it may be justified in calling Lehrfeld's diamino acid *meso*-diaminosuccinic acid (I), and the more soluble diamino acid obtained by Tafel, which yields racemic acid with nitrous acid, is *r*-diaminosuccinic acid (II):



The new dibenzylaminosuccinic acid from *r*-dibromosuccinic acid, on account of its greater solubility, has most probably a structure analogous to that of the *r*-diaminosuccinic acid [(II), where R C<sub>6</sub>H<sub>5</sub>]. It has not been possible to prove this directly, since the benzylamino-acids cannot be converted into the aminoacids or into tartaric acids by any simple means. The simultaneous appearance of the benzylamide of racemic acid (III) cannot be taken as evidence of a racemic configuration for the dibenzylamino-acid, since the former substance is produced by an entirely different reaction (first discovered by Lutz in the case of monobromosuccinic acid), and is not generated from bromofumaric acid, the initial stage in the formation of the dibenzylamino-acid.

The smallness of the yield of racemobenzylamide (one-twentieth

\* It is considered that these designations are more suitable than those used previously, namely, *s*-dibromosuccinic acid and *isodibromosuccinic acid* respectively.

to one-thirtieth of the weight of the isomeric dibenzylamino acid, is probably due to the extreme readiness with which *r*-dibenzylsuccinic acid parts with hydrogen bromide to form bromosuccinic acid.

The action of benzylamine on *r*-dibromosuccinic acid in ether or chloroform solution appears to lead, in the first instance, to the formation of a mixture of mono- and di-benzylamino acids, *r*-bromofumaric acid; the mono-salt being sparingly soluble in water, it may separate out when the mixture is acidified with hydrochloric acid. This salt yields bromofumaric acid and benzylamine hydrochloride when treated with ethereal hydrochloric acid, and when heated with aqueous benzylamine passes into the (*r*)-dibenzylamino acid.\* This reaction may proceed along two different lines, viz., the benzylamine may combine at the double bond to form a benzylamino acid, and the bromine is then displaced by the benzylamino-group, or the bromine is displaced first, yielding a benzylaminofumaric acid,  $\begin{matrix} \text{CO}_2\text{H} \cdot \text{C}(\text{NH} \cdot \text{C}_6\text{H}_5) \\ | \\ \text{H} \cdot \text{C} \cdot \text{CO}_2\text{H} \end{matrix}$ , which then attaches benzylamine to the double bond.

In the previous communication on *meso*-dibromosuccinic acid, it was suggested that the corresponding formation of bromosuccinic acid was followed by the addition of benzylamine at the double bond to yield a bromobenzylamino acid (benzylamine salt) (IV). Further investigations on a product isolated from the reaction mixture, and having this composition,  $\text{C}_{15}\text{H}_{21}\text{O}_4\text{N}_2\text{Br}$ , render it probable that the substance in question is the isomeric dibenzylamine salt of bromomaleic acid (V):



Thus, when treated with ethereal hydrochloric acid, this substance yielded bromomaleic acid and benzylamine hydrochloride (2 mols.), and it appeared to be identical with a product obtained by allowing an alcoholic solution of bromomaleic acid and benzylamine (2 mols.) to crystallise in the cold. These facts render it improbable that we are here dealing with a bromobenzylamino acid.

Investigations, as yet unpublished, by the author in conjunction with H. Webb and C. Mowinkel on the action of anhydrous

\* The terms (*r*-) and (*meso*-) applied to distinguish the two isomeric benzylamino-acids are based on the apparent analogy between these acids and the *r*- and *meso*-diaminesuccinic acids respectively. Incidentally it may be noted that the dibenzylamino acids (*r*-) and (*meso*-) are derived from the corresponding *r*- and *meso*-dibromosuccinic acids, although, of course, this relationship affords no direct proof of the assumed configurations of the dibenzylamino-acids.

as the two dibromosuccinic acids have not resulted in the isolation of bromoaminosuccinic acids,\* only ammonium salts of bromosuccinic and bromofumaric acids being obtained.

It has been found that when the dibenzylamine salt of bromosuccinic acid is heated in aqueous solution it undergoes a reaction, yielding some (*meso*)-dibenzylaminosuccinic † acid, together with a water-soluble substance. When heated in alcoholic solution, the dibenzylamino-acid is accompanied by the monobenzylamine salt of bromosuccinic acid. Circumstances having compelled the author to interrupt these and other investigations proceeding at the University of Birmingham, Edgbaston, it is hoped that in time a further communication may be made in which some light will be thrown on the mechanism of the reaction whereby the bromo-unsaturated acid passes into the saturated dibenzylamino-acid. Reaction products other than the above have been noted in cases where *r*-dibromosuccinic acid has been treated in chloroform solution; these also await further investigation.

#### EXPERIMENTAL.

Eight grams of *r*-dibromosuccinic acid (prepared by McKenzie's method) were treated with 12.4 grams of benzylamine (1 mols.) in 100 c.c. of water, and the mixture was heated to 100° for three hours. An orange-yellow precipitate appeared, which was collected from the cooled mixture and washed with water. The filtrate, on being heated and kept for some time, yielded a further small quantity of precipitate (colourless).

These precipitates contain (*r*)-dibenzylaminosuccinic acid, probably together with some benzylamine salts of the same, also a little dibenzylamido of racemic acid and brown, tarry matter.

#### (*r*)-Dibenzylaminosuccinic Acid.

The precipitates were heated on the steam-bath with dilute aqueous ammonia; a tarry, semi-crystalline residue was separated, and the solution concentrated to a small bulk. The *r*-dibenzylaminosuccinic acid crystallised in flakes and crusts on the surface of the liquid, the yield amounting to 3.9 grams, including a small amount extracted subsequently from the tarry residue. This product was purified by several recrystallisations from dilute ammonia, from which solvent it separated in small, acicular prisms, melting and decomposing, on quick heating, at 250°.‡ Pure (*meso*)-dibenzyl-

\* Claus *Ber.*, 1882, 15, 1849) claims to have isolated the silver salt of a bromo-*r*-succinic acid derived from the action of ammonia on *meso*-dibromosuccinic acid.

† See foregoing note on the (*r*)-dibenzylamino-acid.

‡ All melting points uncorrected.



aminosuccinic acid, when similarly heated, decomposed at 244—247°. (*r*-)Dibenzylaminosuccinic acid is only sparingly soluble in hot water (although considerably more readily soluble than the *meso*-acid), and practically insoluble in alcohol. It dissolves in ammonia on warming and in moderately concentrated hydrochloric acid. Unlike the *meso*-acid, it is not readily precipitated by diluting the acid solution, but separates out on the addition of sodium hydroxide or sodium carbonate solution. The *r*-acid undergoes considerable decomposition on long heating with potassium hydroxide solution, but is little affected by heating in sealed tubes with concentrated aqueous ammonia:

0.0799 gave 97.66 c.c. CO<sub>2</sub> and 5.51 c.c. N<sub>2</sub>.<sup>\*</sup> 0.2004 gave 14.32 c.c. N<sub>2</sub>. C=65.53; N=8.63, 8.56.

C<sub>18</sub>H<sub>20</sub>O<sub>4</sub>N<sub>2</sub> requires C=65.86; N=8.54 per cent.

#### *Dibenzylamide of Racemic Acid.*

The tarry residue separated from the ammoniacal solution of the reaction product (see above) was extracted again with ammonia, and then warmed with a little methyl alcohol. The tar dissolved and a crystalline precipitate remained. This was extracted again with hot ammonia, and the residue weighed 0.18 gram and melted at 207—210°. A further quantity of the same substance (0.05 gram) was obtained from alcoholic washings. The ammoniacal extracts yielded some (*r*-)dibenzylaminosuccinic acid (see above).

The dibenzylamide of racemic acid was purified by recrystallisation from alcohol, from which solvent it separates in glistering, oblong, rectangular plates, some of which have truncated angles forming pentagons and hexagons. It melts at 208—210°.

0.0756 gave 92.73 c.c. CO<sub>2</sub> and 5.28 c.c. N<sub>2</sub>. C=65.70; N=8.53.

C<sub>18</sub>H<sub>20</sub>O<sub>4</sub>N<sub>2</sub> requires C=65.86; N=8.54 per cent.

The dibenzylamide of racemic acid was synthesised by warming dimethyl racemate with benzylamine in methyl-alcoholic solution. The substance crystallised out on the addition of a few crystals of the product obtained from *r*-dibromosuccinic acid. After recrystallisation from absolute ethyl alcohol, the substance presented the same appearance under the microscope as the above-described product, and melted over the same range of temperature (208—210°) as did also a mixture of the two substances. (Found: N=8.53. Calc., N=8.54 per cent.)

The yield of the dibenzylamide from *r*-dibromosuccinic acid is

\* Dry CO<sub>2</sub> and N<sub>2</sub> at N.T.P.; C and N combustion in a vacuum.

smaller than that of the corresponding substance from *meso*-dibromosuccinic acid; 5 grams of the latter substance, when heated with aqueous benzylamine (2 mols.), gave 0.6 gram, and with 1 mol., 0.7 gram of the dibenzylamide of tartaric acid, a purified specimen of which crystallised in rhomboidal plates, accompanied by a few hexagons, and melted at 203°.

A mixture of racemobenzylamide from *r*-dibromosuccinic acid with synthetic *i*-tartarobenzylamide melted at 194°.

*Action of Benzylamine on r-Dibromosuccinic Acid in Non-aqueous Solvents.*

The principal product of the reaction was apparently the benzylamino salt of bromofumaric acid. The amount of benzylamino-acid was again very small.

(a) *Chloroform*.—Five grams of freshly prepared *r*-dibromosuccinic acid (Found, Br 57.11, 57.22. Calc., Br 57.97 per cent.) were treated with a solution of 8 grams of benzylamine in 50 c.c. of chloroform, and heated to boiling under reflux for two hours.

The precipitate (7.1 grams) contained benzylamine hydrobromide, together with less soluble substances. These were separated by treating with water, and eventually by extracting any residual benzylamine hydrobromide with absolute alcohol. The less soluble products (2.8 grams) consisted of benzylamine salts of bromofumaric and (*r*)-dibenzylaminosuccinic acids, together with a little dibenzylamide of racemic acid.

The chloroform mother liquor and washings were evaporated, and the residual tarry residue heated with water. A small amount of (*r*)-dibenzylaminosuccinic acid (0.66 gram, decomposing at 136–138°) was separated, and the solution contained a little benzylamine hydrobromide, together with about 0.3 gram of a product melting and decomposing at 205–225°.

(b) *Alcohol*.—Five grams of *r*-dibromosuccinic acid were dissolved in 20 c.c. of warm absolute ethyl alcohol, and treated with 5 grams of benzylamine. After keeping for about three hours, a crystalline precipitate began to form in the liquid. About sixteen hours later this precipitate was collected, washed with alcohol and with ether, and dried. It weighed 2.6 grams, and melted and decomposed at 172°. An aqueous solution of this substance decolorised cold alkaline permanganate almost instantly, showing the presence of bromofumaric acid. The aqueous solution was slightly cloudy, even on heating, perhaps owing to the presence of a little dibenzylamino-acid.

On acidifying with dilute hydrochloric acid, a crystalline pre-

precipitate appeared, which was collected and recrystallized from water. The substance melted and decomposed at  $219^{\circ}$ , and appeared to be the monobenzylamine salt of bromofumaric acid (see above).

The alcoholic mother liquor and washings on concentration yielded about 1.3 grams of a substance melting at  $200^{\circ}$ , followed by a little (*r*)-dibenzylaminosuccinic acid (decomposing at  $248^{\circ}$ ).

In another experiment, 8 grams of the *r*-dibromosuccinic acid was treated with 16 grams of benzylamine (more than 5 molar), in 120 c.c. of alcohol, and the solution was heated to boiling and reflux for four hours. On concentrating the solution, a crystalline precipitate separated, which was collected and extracted with water. The residue, which was soluble in boiling water, decomposed at  $231^{\circ}$ . This substance is probably the monobenzylamine salt of (*r*)-dibenzylaminosuccinic acid, but cannot readily be parted from possible admixtures of the free acid and its dibenzylamine salt:

0.1425 gave 10.98 c.c.  $N_2$ .  $N=9.61$ .

$C_{18}H_{20}O_4N_2 \cdot C_8H_9N$  requires  $N=9.65$  per cent.

#### *Action of Benzylamine on Bromofumaric Acid.*

The following experiments were carried out with a view to investigate more fully the intermediate products of the reaction between benzylamine and *r*-dibromosuccinic acid. The reaction in this case simplified by the non appearance of the dibenzylamine salt of racemic acid, and by taking a smaller proportion of amine to the acid, the amount of dibenzylamino-acid produced became almost negligible.

A chloroform solution (50 c.c.) of 4.4 grams of bromofumaric acid was treated with 6 grams of benzylamine (2½ molar), and heated to boiling under reflux for three hours. The resulting precipitate weighed 9.3 grams, and a portion dissolved in water contained only a trace of ionic bromine. Theory requires 9.2 grams of the dibenzylamine salt of bromofumaric acid. When the product was dissolved in water, only a very small precipitate remained, but when a large proportion of amine was used (3 molar), this precipitate appeared in greater quantity, and proved to be (*r*)-dibenzylaminosuccinic acid (decomposing at  $242^{\circ}$ ).

The aqueous solution was treated with 3.7 grams of concentrated hydrochloric acid, whereupon a crystalline precipitate was deposited, which was collected, washed with water, alcohol, and ether. The mother liquor was shown to contain benzylamine hydrochloride. The substance, after recrystallisation from water, decomposed at  $221^{\circ}$ , and appeared on analysis to be the monobenzyl-

salt of bromofumaric acid. The yield was 5.75 grams, whilst theory requires 6.8 grams. The substance is rather sparingly soluble in hot water, and almost insoluble in cold water:

0.1238 gave 96.84 c.c.  $\text{CO}_2$  and 4.69 c.c.  $\text{N}_2$ .  $\text{C} = 43.93$ ;  $\text{N} = 4.74$ .  
 $\text{C}_9\text{H}_9\text{O}_4\text{Br}_2\text{N}$  requires  $\text{C} = 43.71$ ;  $\text{N} = 4.61$  per cent.

On the results of this analysis, the substance might equally well be the isomeric bromobenzylaminosuccinic acid,  $\text{C}_9\text{H}_9\text{O}_4\text{NBr}$ , however, the aqueous solution rapidly decolorises cold alkaline permanganate, and when treated with ethereal hydrochloric acid the substance yields benzylamine hydrochloride and bromofumaric acid.

Two grams of the substance were shaken with dry ethereal hydrochloric acid. The precipitate weighed 1 gram, and melted at  $258^\circ$ , whilst theory requires 0.95 gram of benzylamine hydrochloride, the ethereal mother liquor yielded some bromofumaric acid. By continued heating with aqueous benzylamine, the monobenzylamine salt of bromofumaric acid passes into (*r*)-dibenzylaminosuccinic acid.

Thus 1.3 grams of the above-described product were heated at  $100^\circ$  with 1.3 grams of benzylamine in 10 c.c. of water for four hours. The substance gradually dissolved, and, on cooling, a precipitate of small crystals appeared, which weighed 0.25 gram and decomposed at about  $233^\circ$  (compare second experiment with benzylamine on *r*-dibromosuccinic acid). After recrystallisation from dilute ammonia, the substance decomposed at  $242^\circ$  [*r*-dibenzylaminosuccinic acid].

#### *Experiments with meso-Dibromosuccinic Acid.*

These experiments were undertaken with the object of investigating the structure of the compound melting at  $156^\circ$  described in a previous communication (T., 1911, **99**, 1779). It was also thought possible that an intermediate compound might be found between this substance and the final product, (*meso*)-dibenzylaminosuccinic acid.

Seven grams of *meso*-dibromosuccinic acid were treated with 11 grams of benzylamine (4 mols.) in 100 c.c. of absolute ethyl alcohol, and the mixture was heated to boiling for five minutes and then kept overnight. The resulting precipitate weighed 5.6 grams. After extraction with boiling alcohol 0.6 gram remained crude benzylamine salt of (*meso*)-dibenzylaminosuccinic acid. The alcoholic solution on cooling deposited 4.1 grams of the substance melting at  $156^\circ$ , which was investigated as follows: After shaking with dry ethereal hydrochloric acid the resulting precipitate

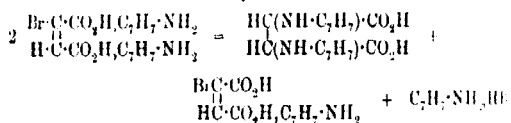
weighed 2.85 grams, and proved to be benzylamine hydrochloride, a specimen melting at  $257^{\circ}$  after recrystallisation from a mixture of alcohol and chloroform. Assuming the substance to be the benzylamine salt of bromomaleic acid, theory requires 2.85 grams of benzylamine hydrochloride, whereas if a bromobenzylamine salt (benzylamine salt) had been present only half this quantity of benzylamine hydrochloride should be obtained.

The ethereal mother liquor deposited colourless crystals of bromomaleic acid, melting at  $138-140^{\circ}$  (Found, Br=41.15. Calc., Br=41.03 per cent.).

A substance melting at  $156^{\circ}$  and apparently identical with the above, except for its more rapid reducing action on permanganate, was obtained by allowing an alcoholic solution of bromomaleic acid and benzylamine (2 mols.) to crystallise in the cold.

The mother liquor from the 4.1 grams of substance mentioned above deposited, on concentration, 0.25 gram of a substance decomposing at  $239-242^{\circ}$ , presumably crude (*meso*)-dibenzylaminosuccinic acid, and then, on the addition of chloroform and further concentration, a precipitate of needle-shaped crystals, which melted at  $142-148^{\circ}$ , and proved on analysis to be the monobenzylamine salt of bromomaleic acid (Found, Br=26.06. Calc., Br=26.04 per cent.) (compare T., 1911, **99**, 1779).

It is suggested that, contrary to what was stated in the preceding communication, the substance melting at  $156^{\circ}$  is the dibenzylamine salt of bromomaleic acid, and that on heating in alcoholic solution it is converted partly into the dibenzylamino-acid with simultaneous formation of the monobenzylamine salt of bromomaleic acid:



In a second experiment 7 grams of *meso*-dibromosuccinic acid were treated with 8.2 grams of benzylamine (more than 3 mols.) in 60 c.c. of absolute ethyl alcohol. The mixture was heated to boiling for five minutes, and then kept for about two and a half hours. The precipitate weighed 3.57 grams, and melted and decomposed at  $142^{\circ}$ . The mother liquor yielded 0.9 gram of coarse needles melting at  $156^{\circ}$  (dibenzylamine salt of bromomaleic acid) and a little nearly pure (*meso*)-dibenzylaminosuccinic acid (decomposes at  $250-254^{\circ}$ ).

The 3.57 grams of substance were dissolved in water, separated from some undissolved dibenzylamino-acid, the solution acidified with hydrochloric acid, and extracted with ether. The ethereal extract yielded some *meso*-dibromosuccinic acid (decomposing at

24—285°; found, Br=58.13. Calc., Br=57.97 per cent.). This shows that the reaction product obtained under these conditions still contains unchanged *meso*-dibromosuccinic acid (as benzylamine salt). A similar result was obtained by heating the acid and amine together for two hours in boiling chloroform solution.

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### CCLXX.—*Some Properties of Solutions of the Boric Acids in Alcohol. A Modified Boiling-point Apparatus.*

By JAMES BRIERLEY FIRTH and JAMES ECKERSLEY MYERS.

THE well-known property of orthoboric acid of imparting a green colour to the alcohol flame has usually been ascribed, at any rate in text-books, to the formation of some organic derivative of boric acid such as triethyl borate.

This idea seems to present considerable theoretical difficulties, and it was with the object of obtaining information on this point, and more particularly of examining the physical properties of alcoholic solutions of the boric acids, that the present work was undertaken.

The first part of the investigation as described in the present communication is devoted to the determination of the boiling points of the solutions and of the composition of the various stillates.

Preliminary experiments indicated that it was extremely probable that the additions of very small proportions of orthoboric acid produced a very slight lowering of the boiling point of ethyl alcohol. This lowering appeared to be of a similar magnitude to that observed by the addition of small quantities of water to alcohol. It was therefore essential that the materials used should be as free from water as possible, and that the experiments should be carried out with the exclusion of water-vapour from the atmosphere.

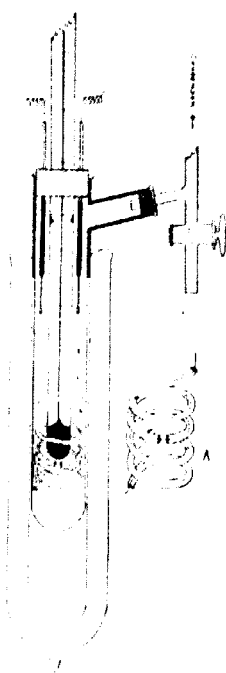
The alcohol was therefore purified, and then dried thoroughly by treatment with metallic calcium or with lime prepared by calcining marble.

Both methods were used, and as there appeared to be no difference in the results obtained, alcohol dried over calcium was employed for the experiments described below. It may be mentioned in passing that in addition to the usual precautions observed

in drying alcohol, the hydrocarbons sometimes found in the alcohol after treatment with calcium were readily and completely removed by distillation from animal charcoal.

The orthoboric acid was purified by several recrystallizations from water; the metaboric acid was prepared by heating the ortho-acid to about  $130^{\circ}$  until decomposition was complete, and the trioxide was obtained by fusing the ortho-acid. In the preparation

FIG. 1.



the glass was ground to a fine powder in an agate mortar. Precautions were taken to exclude moisture from the meta-acid and the anhydride. The three materials were found on analysis to be tolerably pure.

As it was a question of measuring very small differences in boiling point, several kinds of apparatus were tried, and the one described below was eventually used, owing to the unsuitability of the existing types.

The general characteristics of the apparatus, which can be thoroughly recommended for this kind of work, will be clear from the sketch (Fig. 1). The ordinary Beckmann boiling point tube is used, and is enclosed in a Dewar vessel. All exposed glass surfaces are covered with a layer of cotton-lint so as to exclude the heated liquid and vapour from draughts. This precaution is found to be very necessary. The heating is by an electric current of from 2.5 to 3.0 amperes, and is kept steady by means of a rheostat with an ammeter in the circuit.

The current is carried by stout platinum wires, sealed through the glass tubes, in contact with the leads by means of mercury, until it reaches the liquid. The wire is now very much thinner, and is carried through a glass coil made of tubing about 2 mm. in diameter and open at both ends, so that the wire is in contact with the liquid. The glass coil is broken half-way along its length so that it is really two small coils with a gap (A) between them. The two are bound together with platinum wire for convenience

handling and suspending. The gap between the coils should be about 4 mm. The efficiency of the apparatus is largely due to this gap. As the wire becomes heated the liquid inside the narrow tube expands, and rushes out, and is replaced by other liquid, thus causing circulation. This process goes on until boiling point is reached inside the coil, when the circulation becomes more rapid until the whole liquid is at the boiling point and streams of bubbles issue from the various openings in the tube. It will be seen that the enclosure of the wire prevents local superheating common with a bare wire, and the openings in the coil cause rapid and continuous circulation and ebullition.

It is essential that bubbles should appear from the middle and lower openings in the coil. It happens on rare occasions that bubbles issue from the top and middle openings, and then superheating often takes place. In such cases a slight tap will start bubbling from all three points.

With a pure liquid the boiling point, as registered by a Beckmann thermometer, remains steady to  $0.01^{\circ}$  or even to  $0.005^{\circ}$ , so long as the barometric pressure remains steady.

In all experiments a control apparatus was employed containing pure alcohol, so that variations in the boiling point due to barometric changes could be determined and the boiling point of the solution corrected. In the values given below this correction has been included, and all temperatures are expressed in degrees centigrade of an arbitrary Beckmann scale.

TABLE I.

Solute, $H_2BO_3$			Solute, $HBO_2$			Solute, $B_2O_3$		
Gram.	B. p.		Gram.	B. p.		Gram.	B. p.	
of soln.	Change		of soln.	Change		of soln.	Change	
$H_2BO_3$	1.40°	-0.07	0.0036	1.52	-0.04°	0.0049	1.52°	-0.04°
0.0084	1.44	-0.12	0.0074	1.48	-0.08	0.0111	1.36	-0.20
0.0135	1.42	-0.14	0.0140	1.43	-0.13	0.0180	1.36	-0.20
0.0180	1.41	-0.15	0.0200	1.41	-0.15	0.0277	1.38	-0.18
0.0227	1.40	-0.16	0.0261	1.40	-0.16	0.0348	1.46	-0.10
0.0270	1.40	-0.16	0.0311	1.40	-0.16	0.0435	1.61	+0.05
0.0320	1.42	-0.14	0.0375	1.41	-0.15	0.0639	1.98	+0.42
0.0384	1.45	-0.11	0.0457	1.43	-0.13	0.0773	2.25	+0.69
0.0438	1.49	-0.07	0.0520	1.51	-0.05	—	—	—
0.0500	1.52	-0.04	0.0610	1.56	—	—	—	—
0.0548	1.57	+0.01	0.0690	1.61	+0.05	—	—	—
0.0628	1.67	+0.11	0.0800	1.69	+0.13	—	—	—
0.0675	1.75	+0.19	0.1334	2.30	+0.70	—	—	—
0.0740	1.83	+0.27	0.1482	2.62	+1.06	—	—	—
0.0840	1.97	+0.41	—	—	—	—	—	—

Boiling point of pure alcohol  $1.56^{\circ}$ ; volume of alcohol 75 c.c.

It will be clear from the table that there is a lowering of the



boiling point of alcohol on adding either of the three solutes. The lowering reaches a maximum in the case of orthoboric acid when 0.0227 gram-molecule has been added, and then amounts to  $0.16^\circ$ ; in the case of metaboric acid it is  $0.16^\circ$  for 0.0261 gram-molecule, and for the anhydride it is  $0.20^\circ$  for 0.018 gram-molecule. The values given in the table are shown on the graph (Fig. 2) for the sake of comparison.

No further bend or change in the curve was observed up to the point of saturation at boiling point.

The question of the composition of the distillate was next

FIG. 2.

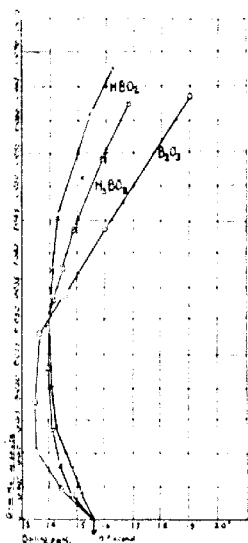
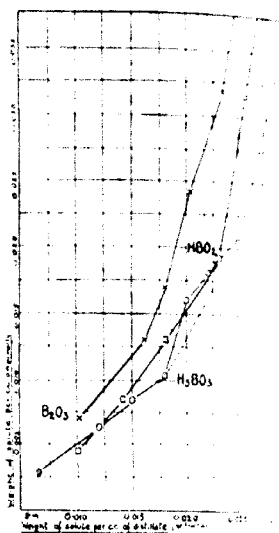


FIG. 3.



examined. The method of distilling is shown in the sketch of the apparatus.

When sufficient time had been allowed for the solute to dissolve completely and the boiling point had become steady, two fractions of the distillate each of 5 c.c. were analysed. The distillate was treated with water, and thus in all cases orthoboric acid was formed, which was titrated with alkali in the presence of glycerol. The assumption was made that the distillate contained, before the addition of water, the original solute. In this connexion it may be remarked that it was frequently observed that after distillation

a small quantity of solid substance appeared in the tubes, etc., of the apparatus after the alcohol had evaporated. This was assumed to be the original solute.

The following table gives the results obtained, the strength of each distillate being expressed in values of the particular solute employed.

A separate experiment was carried out for each strength of solution, not as in the case of the boiling points, where the experiments in each series were made continuous by adding successive amounts of the solute.

TABLE II.

Original volume of alcohol, 75 c.c.

$H_2BO_3$			$HBO_2$			$B_2O_3$		
Weight of $HBO_2$ added.	Weight in 1st fraction.	Weight in 2nd fraction.	Weight of $HBO_2$ added.	Weight in 1st fraction.	Weight in 2nd fraction.	Weight of $B_2O_3$ added.	Weight in 1st fraction.	Weight in 2nd fraction.
0.2530	0.0355	0.0322	0.3300	0.0498	0.0435	0.5230	0.0527	0.0488
0.4860	0.0594	0.0542	0.6430	0.0691	0.0673	0.9355	0.0823	0.0735
0.6348	0.0820	0.0709	0.9810	0.0906	0.0892	1.2770	0.0898	0.0876
0.8170	0.0903	0.0871	1.4510	0.1172	0.1103	1.8020	0.1055	0.1033
1.1990	0.1033	0.1025	2.3890	0.1341	0.1305	2.3730	0.1183	0.1160
1.3700	0.1115	0.1071	3.2830	0.1387	0.1400	3.1140	0.1314	0.1289
1.5880	0.1257	0.1199						
1.6600	0.1276	0.1270						
1.7200	0.1451	0.1412						
1.8530	0.1580	0.1553						

These values are shown in the graph (Fig. 3) for comparison, all weights being expressed in grams of solute per c.c. of solution. In the curve for orthoboric acid the dotted line shows the course which it is considered the curve should take as no reasons can be assigned for the values producing the break. They are probably due to experimental error.

On considering the two sets of curves, the first for the change in boiling point and the second for the volatility of the solutes, it will be noticed that the maximum effect on the boiling point is produced by the solute of minimum volatility, boron trioxide and vice versa with orthoboric acid. In both cases the metaboric acid occupies a middle position in a general way.

Experiments are at present in progress to examine whether the effect of the solute on the vapour pressure is dependent on the temperature, by means of surface-tension measurements and measurements of the heats of solution are being made.

The conclusions drawn from the work described above are as follows:

(1) With certain small concentrations of orthoboric and metaboric acids and boron trioxide, the boiling points of ethyl alcohol solutions are lower than the boiling point of the pure solvent.

(2) The maximum lowering of the boiling point is produced by the least volatile solute, which also has the greatest subsequent effect on the boiling point.

(3) The distillate contains the original solute.

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### CCLXXI.—*Contributions to Our Knowledge of Semicarbazones. Part IV. Action of Hydrogen Chloride.*

By FORSYTH JAMES WILSON, ISIDOR MORRIS HEILBRON, and  
MAGGIE MILLEN JEFFS SUTHERLAND.

IN the course of our investigations on the preparation and properties of some semicarbazones it was found that the presence of hydrochloric acid produced colorations in solutions of some of these substances. As the semicarbazones are, in part, basic compounds it occurred to us that this development of colour might be due to the formation of salts, and in fact experiments instituted to elucidate this point showed that some of these substances do form salts with acids.

The following experiments were carried out to determine under what conditions salts are formed, and to what extent their formation is influenced by the constitution of the semicarbazone. For the most part the investigations have been made on the hydrochlorides of the semicarbazones. Various methods were tried for the preparation of these salts, and it was found that special precautions had to be taken against the presence of moisture, as it is tended, in the presence of hydrochloric acid, to hydrolyse the semicarbazone and give only the aldehyde or ketone and semicarbazide hydrochloride.

In many cases the salt may be prepared by dissolving the semicarbazone in dry chloroform and passing dry hydrogen chloride into the solution. The difficulty in this case is that, if the salt is unstable, exposure to air while filtering brings about decomposition, so that correct results are not obtained. The most satisfactory results were obtained by passing dry hydrogen chloride over the dry substance contained in a U-tube and estimating the quantity of acid added.

Two *piperonyldeneacetonesemicarbazones* were prepared, an  $\alpha$  and a  $\beta$  modification. These isomerides have different melting points and different properties.  $\alpha$ -Piperonyldeneacetonesemicarbazone was exposed to the action of dry hydrogen chloride, and an unstable, crystalline, vermilion salt containing 2.5 molecular proportions of hydrogen chloride was obtained. This salt on exposure to air loses hydrogen chloride, and finally gives a stable, orange *monohydrochloride*.

$\beta$ -Piperonyldeneacetonesemicarbazone gives with hydrogen chloride a stable, yellow *monohydrochloride*, and no further addition can be made to this compound even on continued passage of hydrogen chloride over the dry salt. A slight change in colour is observed, but no addition of acid.

Cinnamaldehydesemicarbazone was next prepared. This semicarbazone exhibits interesting phototropic properties after exposure to bright light. On treating this substance with hydrogen chloride it combines with 2 molecular proportions of hydrogen chloride, and gives an exceedingly unstable, deep orange *compound*. A *sulphate* of this semicarbazone was also prepared, which contained one molecular proportion of sulphuric acid. The sulphate is bright yellow, and stable in ordinary air.

Cinnamaldehydesemicarbazone, an unsaturated compound, might be expected to combine with hydrogen chloride at the double bond, but at least, that the unsaturated nature of the substance would prevent the formation of an additive compound.

The presence of a phenyl group in the semicarbazide radicle evidently influences the absorption of hydrogen chloride, for it was found that *cinnamaldehydephenylsemicarbazone* unites with only one molecular proportion of hydrogen chloride, the *monohydrochloride* thus obtained being yellow. On saturating cinnamaldehydephenylsemicarbazone with bromine a *dibromide*,  $C_{16}H_{15}ON_3Br_2$ , is formed, and this substance does not combine with hydrogen chloride. The addition of bromine therefore prevents salt formation.

A *monobromo-derivative* was prepared from this dibromide by treating with alcohol, when hydrogen bromide was evolved and *monobromocinnamaldehydephenylsemicarbazone*,  $C_{16}H_{14}ON_3Br$ , obtained. This compound combines rapidly with hydrogen chloride, giving a bright yellow salt containing one molecular proportion of hydrogen chloride. On preparing monobromocinnamaldehyde, and then forming the phenylsemicarbazone and passing hydrogen chloride over the compound, a *dihydrochloride* is obtained, which is exceedingly unstable, all the hydrogen chloride being liberated on exposure to air.

Simple semicarbazones, such as acetonesemicarbazone and acetophenonesemicarbazone, also absorb hydrogen chloride, but no color is developed; the substances remain white, but lose their crystalline structure and fall to powder. Acetonesemicarbazone forms a comparatively stable *monohydrochloride*, whereas the addition of hydrogen chloride to acetophenylsemicarbazone reaches a maximum when one and a-half molecular proportions have been taken up. This salt loses hydrogen chloride very rapidly, becoming unstable when half a molecular proportion of hydrogen chloride has been lost, that is, the *monohydrochloride* is comparatively stable. Acetophenonesemicarbazone and acetophenonephenylsemicarbazone were also examined, as these contain more phenyl groups in the molecule, and might be expected to react differently. These substances combined very readily with hydrogen chloride, giving in each case, a yellow *dihydrochloride*, which is exceedingly unstable.

A simple aromatic aldehyde-semicarbazone, such as benzaldehydesemicarbazone, reacts also with hydrogen chloride, giving a stable *monohydrochloride*, which is comparatively stable and only slightly coloured. Benzaldehydephenylsemicarbazone gives a yellow *monohydrochloride*, which is very unstable.

From the results obtained it would seem, first, that the *monohydrochlorides* are for the most part more stable than the *dihydrochlorides*, and, secondly, that the introduction of a phenyl group into the basic part of the molecule of unsaturated semicarbazones diminishes their capacity for addition of hydrogen chloride, whereas in the case of the saturated semicarbazones it increases this capacity. This is shown by a comparison of cinnamaldehydesemicarbazone *dihydrochloride* and cinnamaldehydephenylsemicarbazone *monohydrochloride* with benzaldehydesemicarbazone *monohydrochloride* and benzaldehydephenylsemicarbazone *dihydrochloride*.

We intend to extend these investigations to a larger number of semicarbazones before giving our views on the possible change of structure during addition of acids to semicarbazones, but as circumstances have arisen which render the continuation of the work impossible for the present and as it is uncertain when it will be completed it was thought advisable to record these results.

## EXPERIMENTAL.

### *Piperonylideneacetone semicarbazones.*

Yellow piperonylideneacetone was prepared according to Haber's method (*Ber.*, 1891, **24**, 618). Haber recrystallised his product from alcohol, in which the substance is sparingly soluble, but it was found more convenient to use benzene as the solvent. The

white stereoisomeric piperonylideneacetone was also prepared by Haber's method.

A semicarbazone was prepared from each ketone in the usual manner, and crystallised first from alcohol and finally from chloroform. It was found that the two stereoisomeric ketones gave one and the same semicarbazone, melting at  $217^{\circ}$ , and a mixture of the products showed no depression of the melting point:

0.2020 gave 29.15 c.c.  $N_2$  at  $16^{\circ}$  and 766.5 mm.  $N = 16.85$ .

$C_{12}H_{13}O_3N_3$  requires  $N_2 = 17.0$  per cent.

The semicarbazone forms white crystals, which are insoluble in water, and fairly soluble in hot alcohol or chloroform.

We designate this semicarbazone as the  $\alpha$  modification.

On hydrolysis with hydrochloric or acetic acid the semicarbazone yielded the yellow modification of piperonylideneacetone.

A solution of this  $\alpha$ -semicarbazone in alcohol was exposed to ultraviolet light for thirty hours. The alcohol was then evaporated and the residue fractionally crystallised, first from water and finally from benzene and light petroleum. Besides unaltered substance there was obtained a fairly large quantity of a crystalline substance melting at  $168^{\circ}$ . The substance crystallises in creamy needles, which are more readily soluble in chloroform or alcohol than the  $\alpha$ -semicarbazone. We designate this product the  $\beta$ -modification, since analysis showed it to have the same composition as the  $\alpha$  modification:

0.1400 gave 20.5 c.c.  $N_2$  at  $12^{\circ}$  and 746 mm.  $N = 16.94$ .

$C_{12}H_{13}O_3N_3$  requires  $N = 17.0$  per cent.

#### *Addition of Hydrogen Chloride to the $\alpha$ Modification.*

The reaction was first carried out by passing dry hydrogen chloride into a solution of the substance in dry chloroform. A reddish-orange precipitate separated, which was collected and dried on a porous tile. This substance was very unstable, and easily decomposed by moisture. To determine the amount of hydrogen chloride with which the semicarbazone had combined the substance was warmed with excess of standard alkali, and the residual alkali titrated with standard acid. The results varied with each preparation, but approximated to a compound of the formula



Being to the unsatisfactory nature of the results obtained by this method the following procedure was finally adopted.

A U tube closed by means of glass stopcocks was used. This U tube was specially constructed so that the substance can be exposed to the action of the gas in thin layers. For this purpose instead of the ordinary tube of long limb and narrow bend the

limbs of the U-tube were 8 cm. apart and the limbs only 5 cm. in length.

The tube was first filled with dry air and weighed (weight =  $a$ ). Dry hydrogen chloride was then led into the tube until the weight was constant (weight =  $b$ ). The hydrogen chloride was then displaced by a current of dry air, and a quantity of the semicarbazone introduced into the tube (weight of tube + semicarbazone + air =  $c$ ). Dry hydrogen chloride was then passed through the tube until the weight was constant; this was obtained only after several days. The tube was then closed and weighed. As there was a possibility that the hydrochloride might be unstable in the atmosphere of hydrogen chloride was not displaced, but a correction was made for weighing in such an atmosphere.

Thus: Weight of tube + hydrochloride +  
hydrogen chloride =  $d$ .

Weight of semicarbazone =  $c - a$ .

Weight of hydrochloride =  $d - b$ .

Weight of hydrogen chloride added =  $d - \{c + (b - a)\}$ .

0.3040 semicarbazone gave 0.4198 hydrochloride. HCl added = 27.58.

$C_{12}H_{13}O_3N_3 \cdot 2\frac{1}{2}HCl$  requires HCl = 26.93 per cent.

This salt forms bright, vermilion-coloured crystals. The melting point was indefinite, since decomposition takes place on heating; this occurs at about 125–140°.

If this salt is exposed to light for some days in the tube in which it was weighed the colour changes from vermilion to deep orange without change in weight. In order to prove that the change of colour was not due to slight loss of hydrogen chloride, hydrogen chloride was again passed over the substance, but the orange colour remained unchanged, and the weight was not altered. On prolonged exposure to light the orange-coloured salt acquired a green tint without change in weight. The vermilion colour was not restored either on warming or cooling the substance, or on keeping it in the dark. The experiment was repeated, the semicarbazone this time being subjected to the action of hydrogen chloride in the dark. The same absorption took place, and the vermilion-coloured salt was again obtained:

0.2254 semicarbazone gave 0.3114 hydrochloride. HCl added = 27.61.

$C_{12}H_{13}O_3N_3 \cdot 2\frac{1}{2}HCl$  requires HCl = 26.93 per cent.

This salt on exposure to air at the ordinary temperature rapidly evolves hydrogen chloride. A sample of the salt was exposed to the air at room temperature until, after drying in a desiccator, the weight was constant. For this several weeks were required.

The substance so obtained was orange, but not so deep in colour as the orange salt,  $C_{12}H_{13}O_3N_3 \cdot 2\frac{1}{2}HCl$ , just mentioned. Analysis showed the product to be a *monohydrochloride*.

The substance was warmed gently with excess of  $N/20$ -alkali, and the residual alkali, after filtration, titrated with  $N/20$ -sulphuric acid:

0.1534 required 11.4 c.c.  $N/20$ -NaOH.  $HCl = 13.52$ .

$C_{12}H_{13}O_3N_3 \cdot HCl$  requires  $HCl = 12.83$  per cent.

This orange monohydrochloride is only partly decomposed by water, but is completely decomposed by dilute alkalis. It is apparently quite stable in ordinary air, and in a closed tube it melts and decomposes at  $173-175^\circ$ .

The residue obtained by treatment of the monohydrochloride with alkali was recrystallised from alcohol, and proved to be the *semicarbazone*.

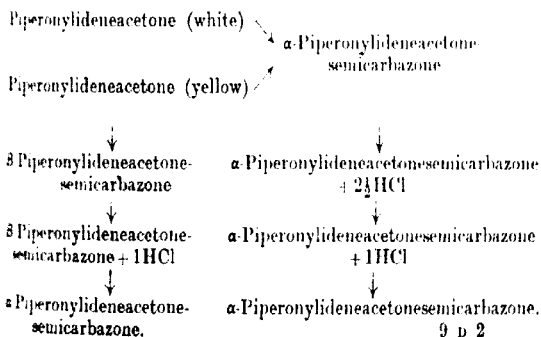
#### Addition of Hydrogen Chloride to the $\beta$ -Semicarbazone.

A solution of the  $\beta$ -semicarbazone in dry chloroform was saturated with dry hydrogen chloride. A yellow, crystalline precipitate separated almost immediately, which was collected, washed with chloroform and light petroleum, dried on a porous tile, and finally in a desiccator. This substance was analysed in the way already described, and proved to be a *monohydrochloride*:

0.3249 required 10.8 c.c.  $N/10$ -NaOH.  $HCl = 13.3$ .

$C_{12}H_{13}O_3N_3 \cdot HCl$  requires  $HCl = 12.9$  per cent.

The monohydrochloride is canary-yellow, melts and decomposes at  $169^\circ$ , is stable in air, and fairly stable towards water. On decomposition with alkali a white substance was obtained, which on crystallisation from alcohol yielded the  $\alpha$ -modification only, and not the  $\beta$ -modification. Hence in this way transformation from the  $\beta$ - into the  $\alpha$ -modification can be effected. Thus:





In order to determine whether this monohydrochloride could combine with more hydrogen chloride a weighed quantity was placed in a U-tube and dry hydrogen chloride passed over it. No increase in weight took place, but the substance acquired a green tinge.

*Cinnamaldehydesemicarbazone.*

This compound was prepared according to Young and Whelan's method (T., 1900, 77, 230). It is white, and, if freshly prepared, undergoes no change of colour in the dark. If, however, it is first exposed to bright light, which produces no visible effect, and then placed in the dark, a yellow colour is developed. This yellow colour disappears on re-exposure of the substance to light. Evidently the freshly prepared substance must first be made active by exposure to intense light before phototropic properties are developed. Further, if either of the active forms is recrystallised, the activity disappears, and exposure to bright light is again necessary to develop phototropic properties. These three modifications all possess the same melting point, namely,  $217^{\circ}$ , which is slightly higher than that recorded in the literature. An alcoholic solution of the semicarbazone was exposed to ultra-violet light for thirty hours. The solution was then concentrated, and the residue fractionally crystallised, but unaltered substance only was obtained.

*Addition of Hydrogen Chloride to the Semicarbazone.*

Owing to the sparing solubility of the substance in all solvents the reaction could not be carried out in solution. Accordingly a weighed quantity was placed in a stoppered U-tube of the form already described, and dry hydrogen chloride passed over the semicarbazone until the weight became constant. The same precautions were taken as in the previous experiments, the substance being weighed in an atmosphere of dry hydrogen chloride and a correction made for the difference in weight of hydrochloride weighed in hydrogen chloride and hydrochloride weighed in air.

0.4148 semicarbazone gave 0.5820 hydrochloride. HCl added 28.11.

$C_{10}H_{13}ON_3 \cdot 2HCl$  requires HCl = 27.86 per cent.

This salt of cinnamaldehydesemicarbazone, which is evidently a dihydrochloride, is deep orange, and very unstable. Moist air immediately decomposes it, with the formation of a viscous compound. During the preparation of the salt the semicarbazone, on first passing hydrogen chloride over it, partly fuses, changes colour to yellowish-orange, and finally the substance becomes powdery and assumes a deep orange colour.

As the dihydrochloride is unstable in ordinary moist air it was transferred from the U-tube to a weighing bottle in dry air in which the salt is comparatively stable. A melting point tube was filled at the same time, sealed, and the melting point found to be  $83-83^{\circ}$ , decomposition also occurring. The apparatus used was a simple but very efficient arrangement, which enabled us to work in dry air with comparative ease.

*Addition of Sulphuric Acid to Cinnamaldehyde semicarbazone.*

A quantity of the semicarbazone was rubbed into a paste with concentrated sulphuric acid, when the mixture became oily and yellow. Dry ether was added, the mixture being kept cool, then just sufficient absolute alcohol to bring the whole into solution, and the mixture placed in ice. On keeping for some time yellow needles crystallised from the solution, which were collected, washed with dry light petroleum, and dried first on a porous tile and finally in a desiccator. Analysis showed the compound to be a salt of sulphuric acid. The analysis was conducted in the same way as in the case of the hydrochlorides, namely, the salt was warmed with excess of *N*/10-alkali and the residual alkali titrated with *N*/10 acid:

0.199 required 7.325 c.c. *N*/10 alkali.  $\text{H}_2\text{SO}_4$  32.92.

$\text{C}_{10}\text{H}_{11}\text{ON}_3 \cdot \text{H}_2\text{SO}_4$  requires  $\text{H}_2\text{SO}_4$  34.1 per cent.

*Preparation of Cinnamaldehyde phenylsemicarbazone.*

Molecular quantities of cinnamaldehyde in alcohol and of phenyl semicarbazide hydrochloride in water were mixed. The solution became deep orange, and a precipitate immediately formed, which was collected, washed with water, and crystallised first from alcohol and finally from a mixture of chloroform and light petroleum.

The phenylsemicarbazone crystallises in white, felted needles, melting at  $205^{\circ}$ . It is readily soluble in chloroform or hot alcohol, and practically insoluble in light petroleum:

0.200 gave 27.2 c.c.  $\text{N}_2$  at  $12^{\circ}$  and 751 mm.  $\text{N} = 15.93$ .

$\text{C}_{16}\text{H}_{15}\text{ON}_3$  requires  $\text{N} = 15.84$  per cent.

The behaviour of the phenylsemicarbazone towards light is exactly the same as that of cinnamaldehydesemicarbazone. The freshly prepared substance is not affected by light or darkness, but if it is exposed to bright light and then placed in the dark a deep yellow colour is developed, which disappears on again exposing to light. Rise of temperature accelerates the conversion of the white into the yellow modification. Thus on exposing a sample of the colourless, inactive modification to light and then placing in a

closed steam-oven the yellow colour becomes apparent almost immediately. If, however, the preliminary exposure to light is omitted, no change of colour is developed by heating the substance in the dark. The melting points of the three modifications were the same, namely, 205°.

A chloroform solution of the phenylsemicarbazone was exposed for thirty hours to ultra-violet light. The solution was carefully examined, but only unchanged substance was obtained.

*Addition of Hydrogen Chloride to Cinnamaldehydephenylsemicarbazone.*

A concentrated solution of the phenylsemicarbazone in dry chloroform was saturated with dry hydrogen chloride. A yellow crystalline precipitate soon separated, which was collected, washed with chloroform, and dried on a porous tile. It was analysed in the usual way, and found to be a *monohydrochloride*:

0.6465 required 20.9 c.c. *N*/10-NaOH. HCl=11.8.

$C_{16}H_{15}ON_3.HCl$  requires HCl=12.11 per cent.

The hydrochloride is canary-yellow, stable in air, and fairly stable towards water. It melts and decomposes at 161–162°. As the semicarbazone of cinnamaldehyde formed a dihydrochloride on passing dry hydrogen chloride over the dry substance it was thought that the phenylsemicarbazone might react with another molecule of hydrogen chloride if exposed to the action of dry hydrogen chloride in the dry state. Accordingly, a quantity of the monohydrochloride was placed in a U-tube and treated as already described in the preparation of other hydrochlorides. After the gas had been passed over the monohydrochloride for several days it was found that no increase in weight had taken place, the substance remaining a monohydrochloride. No change in colour was observed. Starting, however, with cinnamaldehydephenylsemicarbazone (white variety) and passing hydrogen chloride over the dry substance, the gas is rapidly taken up, and the colour becomes deep yellow. After passage of the gas for one week the percentage of hydrogen chloride absorbed was found to be 19.72; thereafter weighing at intervals the hydrogen chloride content appeared to diminish, and after passage of the gas for thirty-eight days the percentage was found to be 17.4. After this the compound continued to lose hydrogen chloride, but at a very slow rate, and with continued passage of the gas would probably approximate to 12.11 per cent. or 1 molecular proportion of hydrogen chloride.

On exposure to air this hydrochloride again gives the stable monohydrochloride:

0.2014 required 6.5 c.c.  $N/10$ -alkali.  $\text{HCl}$  11.79.

$\text{C}_{16}\text{H}_{15}\text{ON}_3\cdot\text{HCl}$  requires  $\text{HCl}$  12.11 per cent.

In the same way the yellow modification of cinnamaldehyde-phenylsemicarbazone was exposed to the action of dry hydrogen chloride in the dark. The yellow compound formed was slightly darker in shade than that from the white modification, and it also reached a maximum addition of hydrogen chloride. The maximum after ten days in this case was 19.46 per cent. The hydrogen chloride content diminished much more rapidly, and in thirty-eight days fell to 15.15 per cent., again an approximation to 1 molecular proportion. On exposure to air this hydrochloride gives, like that of the white modification, a stable monohydrochloride:

0.232 required 7.4 c.c.  $N/10$ - $\text{NaOH}$ .  $\text{HCl}$  11.59.

$\text{C}_{16}\text{H}_{15}\text{ON}_3\cdot\text{HCl}$  requires  $\text{HCl}$  12.11 per cent.

*Addition of Sulphuric Acid to Cinnamaldehydephenylsemicarbazone.*

The phenylsemicarbazone was mixed with a small quantity of concentrated sulphuric acid, alcohol added until the substance dissolved, and the mixture cooled in ice. After a time yellow crystals separated, which were collected and recrystallised from glacial acetic acid. The sulphate was analysed in the usual way by heating gently with excess of standard alkali and titrating the residual alkali:

0.100 required 11.1 c.c.  $N/10$   $\text{NaOH}$ .  $\text{H}_2\text{SO}_4$  27.2.

$\text{C}_{16}\text{H}_{15}\text{ON}_3\cdot\text{H}_2\text{SO}_4$  requires  $\text{H}_2\text{SO}_4$  26.99 per cent.

The sulphate is a brilliant, yellow-coloured powder, stable in air, but easily decomposed by cold water and dilute alkali with the formation of the phenylsemicarbazone and sulphuric acid.

*Preparation of a Dibromide of Cinnamaldehydephenylsemicarbazone.*

The theoretical quantity of dry bromine in dry chloroform was added to the phenylsemicarbazone dissolved in dry chloroform, and the mixture was allowed to remain for half an hour, when yellow crystals began to appear. When all the substance had crystallised out the crystals were collected, dried, and recrystallised from chloroform. The substance crystallises in canary-yellow needles, which are very sparingly soluble in chloroform, and melt at  $187^\circ$ . Analysis showed it to be the dibromide of cinnamaldehydephenylsemicarbazone:

0.200 gave 17.1 c.c.  $\text{N}_2$  at  $10^\circ$  and 754 mm.  $\text{N} = 10.14$ .

$\text{C}_{16}\text{H}_{15}\text{ON}_3\text{Br}_2$  requires  $\text{N} = 9.91$  per cent.

This dibromide was subjected to the action of dry hydrogen chloride, but no addition took place. Evidently the dibromide does not form a hydrochloride. Also on treating cinnamaldehydephenylsemicarbazone monohydrochloride with bromine in ether solution and adding light petroleum a yellow precipitate was obtained, which consists of the dibromide of cinnamaldehydephenylsemicarbazone.

*Preparation of a Monobromo-derivative of Cinnamaldehydephenylsemicarbazone from the Dibromide.*

It was found that on recrystallisation from alcohol the dibromide was decomposed, hydrogen bromide being liberated and a white substance melting at  $168^{\circ}$  crystallising out. Some of the cinnamaldehydephenylsemicarbazone dibromide was therefore heated in alcohol until dissolved, then diluted with water, and the product allowed to crystallise:

0.200 gava 21.05 c.c.  $N_2$  at  $12^{\circ}$  and 739 mm.  $N=12.15$ .

$C_{16}H_{14}ON_3Br$  requires  $N=12.20$  per cent.

The substance obtained is therefore a monobromo-derivative of cinnamaldehydephenylsemicarbazone. It crystallises in small colourless, glistening needles, which after several crystallisations melt at  $195^{\circ}$ . It is readily soluble in chloroform, benzene, or boiling alcohol, but practically insoluble in light petroleum.

*Addition of Hydrogen Chloride to the Monobromo-derivative of Cinnamaldehydephenylsemicarbazone.*

A weighed quantity of the monobromo-derivative was placed in a U tube and subjected to the action of hydrogen chloride in the manner already described. Reaction took place immediately, and a yellow salt was produced. Passage of the gas was continued until the weight became constant:

0.6624 monobromo-derivative gave 0.7458 hydrochloride.  $HCl$  added = 11.18.

$C_{16}H_{14}ON_3Br.HCl$  requires  $HCl=9.59$  per cent.

The hydrochloride is bright canary-yellow, and fairly stable in air, gradually losing hydrogen chloride. It is partly decomposed by water and completely by dilute alkali.

*Preparation of Monobromocinnamaldehydephenylsemicarbazone.*

Cinnamaldehyde was first brominated according to the method described by Zincke and Hagen (*Ber.*, 1884, 17, 1815). The brominated product separated at once, and was crystallised from

alcohol. It was mixed with the necessary quantity of phenylsemicarbazide in alcoholic solution, when the *phenylsemicarbazone* separated immediately and was crystallised from alcohol:

0.250 gave 26.2 c.c.  $N_2$  at  $12^\circ$  and 745 mm.  $N = 12.13$ .

$C_{16}H_{14}ON_3Br$  requires  $N = 12.22$  per cent.

The substance crystallises in flat, colourless prisms, melting at  $197^\circ$ . It is soluble in alcohol or chloroform, but more readily soluble in the latter than is the monobromo compound derived from the dibromide. It is not identical with the latter substance, as is shown by crystalline structure, solubility, and melting point.

*Addition of Hydrogen Chloride to the above Monobromocinnamaldehydephenylsemicarbazone.*

Hydrogen chloride was passed over a weighed quantity of the substance until the weight became constant. The addition of hydrogen chloride took place at once, but several days elapsed before the weight became constant:

0.5922 phenylsemicarbazone gave 0.713 hydrochloride.  $HCl$  added = 16.94.

$C_{16}H_{14}ON_3Br \cdot 2HCl$  requires  $HCl = 17.50$  per cent.

This *dihydrochloride* of monobromocinnamaldehydephenylsemicarbazone is bright yellow, of a slightly deeper shade than the monohydrochloride of the monobromo compound obtained from cinnamaldehydephenylsemicarbazone dibromide. It is, however, much more unstable, and on keeping even in a stoppered weighing bottle loses hydrogen chloride, the colour at the same time disappearing. A portion of the salt was exposed to the air for some time, then dried in a desiccator, and weighed. This treatment was repeated until the weight was constant, which condition was reached at the end of three weeks, and the yellow colour had entirely disappeared. On titrating a weighed quantity of the substance with standard alkali it was found that the hydrochloride had lost the whole of the hydrogen chloride on exposure to the air.

*Addition of Hydrogen Chloride to Acetonesemicarbazone.*

Dry hydrogen chloride was passed over a weighed quantity of acetonesemicarbazone (m. p.  $187^\circ$ ) in the manner previously adopted. Hydrogen chloride was absorbed at once, and the substance fused slightly, although no change in colour occurred. After some time the substance became powdery, the U-tube was weighed, and increase in weight found to have taken place. Hydrogen chloride was then passed over the substance until the weight became constant:

1.1984 acetonesemicarbazone gave 1.5820 hydrochloride.  $H_2O$  added = 24.24.

$C_4H_5ON_3.HCl$  requires  $HCl = 24.09$  per cent.

The hydrochloride is evidently a monohydrochloride, and is obtained as a white powder, melting in a closed tube at  $150-160^\circ C$ . It is unstable in ordinary air, and hydrogen chloride is gradually evolved from it. In dry air it is comparatively stable.

*Addition of Hydrogen Chloride to Acetophenylsemicarbazone.*

Dry hydrogen chloride was passed over a weighed quantity of acetophenylsemicarbazone (m. p.  $157^\circ$ ) as before until the weight was constant. The substance caked slightly on the first addition of hydrogen chloride, but ultimately became powdery. No colour was produced, but an addition in weight occurred, showing the formation of a salt:

1.1088 phenylsemicarbazone gave 1.4180 hydrochloride.  $H_2O$  added = 21.80.

$C_{10}H_{13}ON_3.HCl$  requires  $HCl = 16.05$  per cent.

$C_{10}H_{13}ON_3.1\frac{1}{2}HCl$  „  $HCl = 22.26$  „ „

On exposure to air it rapidly loses hydrogen chloride.

*Addition of Hydrogen Chloride to Acetophenonesemicarbazone.*

Dry hydrogen chloride was passed over a weighed quantity of the semicarbazone (m. p.  $202^\circ$ ) as before. The substance fused almost immediately and a yellow colour was developed. The weight increased gradually, but did not become constant, and the substance remained semi-solid, and appeared to decompose. The amount of hydrogen chloride taken up approximated to two molecular proportions, but the results could not be trusted owing to the sensitive condition of the substance.

*Addition of Hydrogen Chloride to Acetophenophenylsemicarbazone.*

This compound behaved in much the same way as the semicarbazone. Addition of hydrogen chloride takes place with fusion, and a deep yellow colour is developed. The effect of strong cooling was tried in this case, the tube being surrounded by carbon dioxide snow. Even under these conditions the substance fused, although the colour developed was very much less. In the case of this phenylsemicarbazone the hydrochloride solidified to a hard mass adhering to the tube.

Two experiments were tried: (1) Addition of dry hydrogen chloride at room temperature:

0.5932 phenylsemicarbazone gave 0.7808 hydrochloride. HCl added = 24.02.

$C_{13}H_{13}ON_3 \cdot 2HCl$  requires HCl = 22.36 per cent.

(2) Addition of hydrogen chloride at the temperature of solid carbon dioxide:

0.3272 phenylsemicarbazone gave 0.4094 hydrochloride. HCl added = 20.05.

*Addition of Hydrogen Chloride to Benzaldehydesemicarbazone.*

Hydrogen chloride was passed over the semicarbazone (m. p.  $222^\circ$ ) in the manner already described. The colour changed from white to greyish-white, and slight fusion took place on the first formation of the monohydrochloride:

0.8548 semicarbazone gave 1.0613 hydrochloride. HCl added = 19.45.

$C_8H_9ON_3 \cdot HCl$  requires HCl = 18.29 per cent.

The hydrochloride is greyish-white, melts at  $199^\circ$ , and is fairly stable in air.

*Addition of Hydrogen Chloride to Benzaldehydephenylsemicarbazone.*

The phenylsemicarbazone was dissolved in dry chloroform, and dry hydrogen chloride passed through the solution. The solution became yellow, and a white precipitate formed, which was collected in an atmosphere of dry air, washed with chloroform, and dried on a porous tile. A quantity of this was placed in a dry, previously weighed weighing-bottle, the bottle weighed, and the contents were shaken into excess of standard alkali; the excess of alkali after warming the mixture was titrated with standard acid:

0.2598 required 13.3 c.c.  $N/10$ -NaOH. HCl = 18.68.

$C_{14}H_{13}ON_3 \cdot 2HCl$  requires HCl = 23.4 per cent.

The hydrochloride evidently loses hydrogen chloride too rapidly even in dry air to allow of accurate estimation.

The substance was therefore exposed to the action of dry hydrogen chloride until the weight became constant. The substance became yellow immediately on the passage of the gas, and at the same time partly liquefied. The final product was deep yellow and semisolid in appearance.

Owing to fusion having taken place a satisfactory result was not obtained:

0.3264 phenylsemicarbazone gave 0.4196 hydrochloride. HCl added = 22.21.

$C_{14}H_{13}ON_3 \cdot 2HCl$  requires HCl = 23.4 per cent.



# 2906 CONTRIBUTIONS TO OUR KNOWLEDGE OF SEMICARBAZONES

This dihydrochloride is yellow and exceedingly unstable, decomposes immediately on exposure to air.

Annexed is a summary of the compounds examined.

Substances investigated	Mols. HCl added.	Colour of additive product.	Stability of additive product.
$\alpha$ -Piperonylideneacetone-semicarbazone	2	Vermilion	Very unstable, affected by heat, stable at 1 mm HCl.
$\beta$ -Piperonylideneacetone-semicarbazone	1	Canary-yellow	Stable.
Cinnamaldehyde-semicarbazone	2	Deep orange	Unstable.
Cinnamaldehydephenyl-semicarbazone	1	Canary-yellow	Stable.
Cinnamaldehydephenyl-semicarbazone dibromide	No addition	—	—
Monobromo-derivative from cinnamaldehydephenylsemicarbazone dibromide	1	Yellow	Fairly stable, gradually loses HCl.
Monobromocinnamaldehyde-semicarbazone	2	Bright yellow	Unstable.
Acetone-semicarbazone	1	No colour	Comparatively stable in dry air, HCl evolved slowly on drying in air.
Acetonephenylsemicarbazone	1½	No colour	Unstable, no stability at 1 mm HCl.
Acetophenonesemicarbazone	2	Yellow	Unstable.
Acetophenonephenyl-semicarbazone	2 (indefinite)	Yellow	Unstable.
Benzaldehydesemicarbazone	1	Greyish	Fairly stable.
Benzaldehydephenyl-semicarbazone	2	Yellow	Exceedingly stable.

In conclusion, we desire to express our thanks to the Carnegie Trust for the Universities of Scotland for a grant which defrays the expenses of the work. We also desire to record our thanks to Professor G. G. Henderson for the interest he has taken in these investigations.

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## CLXXII.—*The Absorption Spectra of Sulphurous Acid and Sulphites.*

By ROBERT WRIGHT.

In a former paper (this vol., p. 669) dealing with the relation between the absorption spectra of various acids and their alkali salts, the absorption curves of sulphurous acid and sodium sulphite were shown. In view of the doubtful constitution of these substances, and as their light absorptive powers are so fundamentally different, the acid showing selective, and the salt only general absorption; it was considered of importance to investigate their special case more closely.

Potassium sodium sulphite, prepared either from sodium hydrogen sulphite and potassium hydroxide or from potassium hydrogen sulphite and sodium hydroxide, gave a spectrum identical with that of sodium sulphite.

Most sulphites of the bivalent metals are too insoluble to admit of investigation; magnesium sulphite is, however, sparingly soluble, and on photographing its  $M/100$  solution it was found to give the same spectrum as the alkali sulphites.

It seemed possible that sulphurous acid might have a structure similar to that of the sulphonic acids, for it will be seen on reference to the paper already mentioned that benzenesulphonic acid and its salt both give a band in the same region of the spectrum, but at a greater dilution than sulphurous acid. On examination, however, the sodium salt of ethylsulphonic acid was found to be quite diactinic, so that the occurrence of the band in the aromatic compound must be attributed to the phenyl nucleus, which, as is well known, almost invariably causes selective absorption.

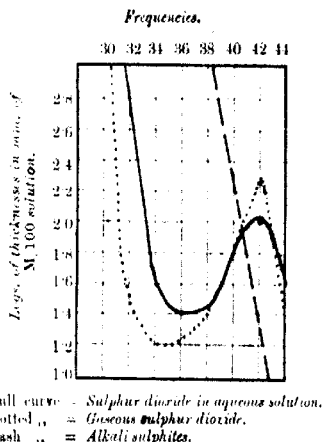
Ethyl sulphite, from thionyl chloride, was also examined in alcoholic solution, and was found to be practically diactinic at  $M/100$  dilution.

Stewart and Macbeth, in an unpublished research, observed that aqueous sulphur dioxide gave a band in the ultra-violet. It was therefore thought advisable to compare this band with that of aqueous sulphurous acid.

The investigation was carried out by means of the following apparatus. A tube of about 2 cm. in diameter and exactly 10 cm. long has its ends closed with quartz windows. This observation cell has two side-tubes, one connected with a source of the gas and the other with a manometer and pump. The apparatus is fitted with three taps, one between the source of the gas and the cell,

one between the cell and the manometer, and the third between the manometer and pump. All connexions in the apparatus are of glass.

In using the apparatus, all the taps are opened and the air is swept out by a stream of sulphur dioxide; the taps are now closed, the apparatus is connected with the pump, and a series of photographs taken through the cell at different pressures, which are observed by means of the manometer. Taking 2.9266 grams as the weight of a litre of sulphur dioxide at N.T.P., the normality of the gas under these standard conditions is  $2.9266/64 = 0.04572N$ . A thickness of 100 mm. of a gas the normality of which is 0.04572 corresponds with 4.57 mm. of *N*-concentration. By a similar calculation



lation the 10 cm. thicknesses at different pressures can be reduced to the corresponding thicknesses of *N*-gas. The curve drawn from these results is shown in comparison with that of aqueous sulphurous acid, and it will be seen that they strongly resemble one another: for although differing slightly in persistence, they correspond in their positions in the spectrum and in the thicknesses at which they occur.

A few comparison photographs were also made, using air as a diluent. For this purpose the tube was filled with gas as before, the pressure reduced, and a photograph taken; air was now admitted to the cell by raising a tap out of its seat, and a second exposure made. Since the gas in the cell is under less than atmospheric pressure, it cannot escape during this process, and so the

second exposure is made through the same amount of sulphur dioxide as the first; only, in the latter case it is diluted with air instead of being under diminished pressure. In the half-dozen comparisons made no difference could be detected between the two sets of photographs.

The result seems to indicate that aqueous sulphurous acid consists largely of uncombined sulphur dioxide molecules. The solution was also examined at zero, by surrounding the cell with ice, in order to see if the solution of the crystalline compound which separates at that temperature gave the same spectrum as the solution under ordinary conditions. No difference in the two spectra could be detected.

From this work the conclusion may be drawn that an aqueous solution of sulphur dioxide consists to a large extent of uncombined gas molecules.

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PRINTED IN GREAT BRITAIN BY  
EDWARD CLAY AND SONS, LIMITED,  
PRESWELL STREET, STAMFORD STREET, S.E.,  
AND BUNDA, SURREY.

## Organic Chemistry.

**Composition of Mid-Continental (American) Petroleum.** F. W. BUSHONG (*J. Ind. Eng. Chem.*, 1914, 6, 888—890).—Crude oil from the wells of the Alluwe Oil Co., Oklahoma, was submitted to fractional distillation, the fractions being collected separately for each difference of 2° in the boiling point between 60° and 300°; the physical constants of these fractions are recorded. The total gasoline fraction, b. p. 40° to 150°, amounted to 13.77%, and the kerosene fraction, b. p. 150° to 300°, to 28.80%. Ozonides were separated from some of the fractions similar to those obtained by Molinari and Fenaroli from Russian and Roumanian petroleum (A., 1908, i, 933). W. P. S.

**A Crystalline Compound of Isoprene with Sulphur Dioxide.** G. DE BAUM (*Proc. K. Akad. Wetensch. Amsterdam*, 1914, 17, 585—586).—When isoprene is mixed with an equal volume of liquid sulphur dioxide, a crystalline substance of the composition  $C_5H_8SO_2$  separates after one or two days. It may be purified by recrystallisation from ethyl ether and melts without decomposition at 62.5°. According to freezing point measurements, it dissolves unchanged in benzene. When dissolved in carbon tetrachloride or ethyl ether, it is only slowly acted on by bromine, but reacts quickly with alkaline potassium permanganate. H. M. D.

**The So-called "Acetone-soluble Phosphatides."** HUGH MACLEAN (*Biochem. J.*, 1914, 8, 453—459. Compare Fränkel and Ari, A., 1909, i, 620).—The author shows that the so-called acetone-soluble phosphatide obtained from the heart of the ox is impure lecithin. The lecithin can be separated from the accompanying fats and fatty acids by the addition of a small amount of an electrolyte such as calcium chloride to the acetone solution. The precipitate, when purified, has all the reactions of lecithin and is insoluble in acetone. The author considers it probable that all the acetone-soluble phosphatides described in the literature consist of lecithin contaminated with a nitrogenous impurity. H. W. B.

**Brain Kephalin. I. Distribution of the Nitrogenous Hydrolysis Products of Kephalin.** C. G. MACARTHUR (*J. Amer. Chem. Soc.*, 1914, 36, 2397—2401).—An account is given of a method for extracting kephalin from sheep's brains and the hydrolysis of the product.

The hydrolysis was effected by boiling the kephalin with 1% hydrochloric acid for twenty hours. The nitrogen in the residue was estimated and is referred to as "residual nitrogen." The ammonia nitrogen was estimated in the usual way, the total amino-nitrogen by means of the amino-apparatus described by van Slyke (A., 1912, ii, 908), and the amino-acid nitrogen by Kober's copper method (A., 1913, 990). The results were as follows: residual nitrogen, about 0.20%;

ammonia nitrogen, about 0.20%; amino-alcohol nitrogen (difference between the total amino-nitrogen and the amino-acid nitrogen), 0.56%, and amino-acid nitrogen, 0.40%.

Kephalin contains neither choline nor neurine. Ordinary kephalin consists of at least two kephalins which contain the larger proportions of their nitrogen in the form of amino-alcohol and amino-acid respectively.

E. G.

**Action of Selenium Bromide on Magnesium Alkyl Compounds.** A. PIERONI and C. COLI (*Gazzetta*, 1914, 44, ii, 349–355).—Attempts to introduce selenium into hydroxybenzoxonitrile and hydroxynaphthonitrile, etc., by treatment with hydrogen selenide, and into oxanilide, by heating with phosphorus pentaselenide, were unsuccessful, but it was found that selenium bromide reacts with organo-magnesium derivatives.

With dimagnesium acetylene dibromide (compare *Locitech*, this vol. i, 405), the reaction does not follow the normal course, but seems to proceed according to the equation:  $3\text{MgBr}\cdot\text{C}\equiv\text{C}\cdot\text{MgBr} + 4\text{Se}_2\text{Br}_2 + 2\text{H}_2\text{O} = \text{OH}\cdot\text{Se}\cdot\text{C}\equiv\text{C}\cdot\text{Se}\cdot\text{C}\equiv\text{C}\cdot\text{Se}\cdot\text{C}\equiv\text{C}\cdot\text{Se}\cdot\text{OH} + 6\text{MgBr}_2 + \text{Se}_2 + 2\text{HBr}$ . The compound thus formed was obtained only in an impure condition as a brown powder.

With magnesium ethyl bromide, the reaction takes place as follows: (1)  $\text{Se}_2\text{Br}_2 + 2\text{MgEtBr} = \text{Se}_2\text{Et}_2 + 2\text{MgBr}_2$ ; (2)  $\text{Se}_2\text{Et}_2 + \text{EtBr} =$

$\text{SeEt}_2\cdot\text{Br}\cdot\text{SeEt}_2$

and (3) the latter +  $\text{MgEtBr} + \text{H}_2\text{O} = \text{SeEt}_2\cdot\text{SeH} + \text{MgBr}_2 + \text{EtOH}$ . Triethylselenitine hydroselenide,  $\text{SeEt}_2\cdot\text{SeH}$ , thus obtained, is a dense, yellow oil of disagreeable odour; with alcoholic silver nitrate it gives up part of its selenium as silver selenide, and with hydrochloric-platinic acid it forms a crystalline product, which has been obtained only in small amount and has not been purified.

T. H. P.

**Equilibrium in the System, Lead Acetate, Lead Oxide, Water, at 25°.** RICHARD F. JACKSON (*J. Amer. Chem. Soc.*, 1914, 36, 2346–2357).—In view of the fact that comparatively little modern work has been done on the basic lead acetates, an investigation has been carried out on the basis of the phase rule in order to ascertain the compounds capable of existence and their relative stability.

Mixtures of lead acetate, lead oxide, and water were shaken in flasks kept in a thermostat at 25° for at least forty-eight hours. After equilibrium had been attained, the solid phase was removed and the composition and density of the solution were determined. The results show that three solid phases are capable of existence. Normal lead acetate,  $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2\cdot 3\text{H}_2\text{O}$ , forms brilliant, monoclinic crystals, and is soluble in water to the extent of 35.50% at 25°. Its compound,  $3\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2\cdot\text{PbO}\cdot 3\text{H}_2\text{O}$ , crystallises in needles and is exceedingly soluble in water, yielding solutions with  $D_4^{25}$  1.93–2.2; it is unstable and can only exist in presence of excess of dissolved basic lead acetate. The compound,  $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2\cdot 2\text{PbO}\cdot 4\text{H}_2\text{O}$ , forms minute needles, and is stable in contact with solutions of itself, but under such conditions has a solubility of only 13.3%. Saturation curves

have been constructed and a new theory of the course of such curves is put forward. E. G.

**Structure of Maltose and its Oxidation Products with Alkaline Hydrogen Peroxide.** W. LEE LEWIS and SIEGEL A. BUCKBOROUGH (*J. Amer. Chem. Soc.*, 1914, 36, 2385—2397).—Lewis (A., 1909, i, 767) investigated the action of Fehling's solution on maltose, but the results failed to elucidate the constitution of the sugar as the oxidation did not proceed far enough.

The present work was undertaken in the hope that alkaline hydrogen peroxide might effect a more complete destruction of the maltose molecule and permit a better quantitative separation of the products. It has been found that the formation of saccharinic acid does not take place under these conditions. The ratio and nature of the oxidation products are quite different from those of dextrose with the same reagent, this difference being due to the effect of the glucoside bond. About half the maltose is oxidised as such, whilst the remainder seems to be hydrolysed before being oxidised.

From 100 grams of anhydrous maltose there were obtained 22.97 grams of hydrolysed dextrose, 0.16 gram of mannolactone, 16.04 grams of glycollic acid, 0.11 gram of oxalic acid, 55.37 grams of formic acid, and 4.44 grams of carbon dioxide, together with 1.18 grams of other substances, which probably included erythronic and *L*-threonic acids.

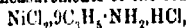
The formation of glucosido-acids in the oxidation of maltose affords an explanation of the fact that a molecule of dextrose requires 2.48 atoms of oxygen by Fehling's solution whilst the large maltose molecule requires only 2.86 atoms. The formation of  $\alpha$ - and  $\beta$ -isosaccharinic acids from maltose under the influence of alkali hydroxide involves the three hydroxyl groups attached to the first, second, and third carbon atoms from the free aldehyde group, and these carbon atoms must be present in the original maltose molecule, and their participation in the glucoside union is therefore precluded. The formation, in the oxidation of maltose, of relatively large amounts of  $\gamma$ -*D*-glucosido-glycollic acid, rather than  $\gamma$ -*D*-glucosidoglyceric acid, indicates that the terminal or primary alcohol carbon atom functions in the glucoside union of the two dextrose molecules. Maltose, therefore, is a  $\gamma$ -*D*-glucosidodextrose with the glucoside union on the primary alcohol carbon atom. It is probable that, under the influence of alkali hydroxide, maltose enters into an equilibrium of the six glucosido-hexoses of the dextrose series, and that the various oxidation products found result from the dissociation and oxidation of the intermediate hexose-dienols. E. G.

**Effect of Pressure on Yields of Products in the Destructive Distillation of Hardwood.** R. C. PALMER (*J. Ind. Eng. Chem.*, 1914, 6, 890—893).—Destructive distillations of birch and maple woods under increasing pressure result in a slight increase in the yield of alcohol, charcoal, and gas, whilst the quantities of acetic acid, pyroligneous liquor, and tar are decreased. The maximum effect on all the products is obtained with a pressure of 60 lbs. per square



inch, the most decided effect being noticed in the tar, which is diminished to the extent of 60 to 65%. Distillations were also made at pressures as high as 450 lbs. per square inch, but the exothermic reaction was so violent that the experiments were discontinued. At this pressure, the concentration of the dissolved tar in the pyroligneous liquor was so low that redistillation was not necessary in order to titrate the acidity; in practical operation, the first distillation of the primary liquor would not be necessary in order to make grey acetate of lime. It is possible, therefore, that pyroligneous acid, free from soluble tar, might be obtained by subjecting the distillate to a high pressure during the vapour stage. W. P. S.

**Compounds of Salts of Nickel and of Allylamine.** A. PIZZOSI and A. PINOTTI (*Gazzetta*, 1914, 44, ii, 366—373).—The authors have endeavoured to ascertain the influence of aliphatic double linkings on the co-ordination numbers of complex salts by investigating double salts of nickel and allylamine. In no case, however, do these salts contain latent nickel in complex union; they decompose in aqueous solution, and the ions of the component salts are revealed by their reagents. Cryoscopic measurements of the compound,



in water indicate a molecular weight of 46.29 instead of the calculated value, 972.73, so that the compound forms twenty-one ions. The other compounds described undergo hydrolysis in aqueous solution with formation of nickelous hydroxide.

The compound,  $\text{NiCl}_2 \cdot 9\text{C}_3\text{H}_5 \cdot \text{NH}_2 \cdot \text{HCl}$ , obtained by saturating allylamine with nickel chloride previously dried at  $140^\circ$ , forms extremely deliquescent, square plates of an intense red colour, which is changed to yellow by traces of moisture. It has a neutral reaction and a strong taste, and exhibits marked chromoisomerism, becoming blue when heated and resuming its red colour when cool.

The compound,  $\text{NiCl}_2 \cdot 7\text{C}_3\text{H}_5 \cdot \text{NH}_2$ , or  $[\text{Ni}(\text{C}_3\text{H}_5 \cdot \text{NH}_2)_4]_2\text{Cl}_2 + 3\text{C}_3\text{H}_5 \cdot \text{NH}_2$ , obtained by saturating allylamine with nickel chloride dried at  $140^\circ$ , the mass being kept cool, forms square, blue plates and loses  $3\text{C}_3\text{H}_5 \cdot \text{NH}_2$  in a vacuum over sulphuric acid, the resultant green compound,  $[\text{Ni}(\text{C}_3\text{H}_5 \cdot \text{NH}_2)_4]_2\text{Cl}_2$ , resembling nickelous hydroxide in appearance.

The compound,  $[\text{Ni}(\text{C}_3\text{H}_5 \cdot \text{NH}_2)_3]_2\text{SO}_4$ , prepared by the interaction of nickel sulphate and allylamine in presence of water, forms square, blue plates and effloresces and loses  $2\text{C}_3\text{H}_5 \cdot \text{NH}_2$  in the air; the residual compound,  $[\text{Ni}(\text{C}_3\text{H}_5 \cdot \text{NH}_2)_3]_2\text{SO}_4$ , is an almost odourless green powder, which is decomposed by water. Treatment of the compound,  $\text{NiSO}_4 \cdot 5\text{C}_3\text{H}_5 \cdot \text{NH}_2$ , with concentrated hydrochloric acid yields the compound,  $\text{NiCl}_2 \cdot 9\text{C}_3\text{H}_5 \cdot \text{NH}_2 \cdot \text{HCl}$  (see above). T. H. P.

**Organic Fluorine Derivatives.** I. J. RINKES (*Chem. Weekblad*, 1914, 11, 952—956. Compare this vol., i, 679).—Chlorination of *p*-fluoronitrobenzene in the presence of ferric chloride yields 4-fluoro-3-chloro-1-nitrobenzene, b. p.  $227-232^\circ$ , m. p.  $41^\circ$ , which is volatile with steam. Reduction with tin and hydrochloric acid

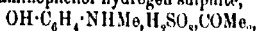
converts it into 4-fluoro-3-chloroaniline, plates, m. p.  $43.9^{\circ}$ , which decomposes on distillation. Diazotisation converts this product into *o*-fluorochlorobenzene, b. p.  $138.5^{\circ}/774$  mm., m. p.  $-42.5^{\circ}$ , which is volatile with steam.

*p*-Fluoroanisole, prepared from diazotised *p*-anisidine, cannot be readily purified; however, by heating with aluminium chloride at  $130^{\circ}$ , it yields *p*-fluorophenol, m. p.  $46.5^{\circ}$  (compare Swarts, A., 1913, i, 841), which in alkaline solution is re-converted by methyl sulphate into *p*-fluoroanisole, b. p.  $157.1^{\circ}/767$  mm., m. p.  $-43.5^{\circ}$ .

Sodium persulphate oxidises *p*-fluoroaniline to *p*-fluoronitrosobenzene, m. p.  $35.2^{\circ}$ , which is volatile with steam. This substance reacts with *p*-fluoroaniline in solution in glacial acetic acid to form 4:4'-difluoroazobenzene, orange-red needles, m. p.  $101.1^{\circ}$ .  
A. J. W.

Action of Nitric Acid on the Three Isomeric Fluorotoluenes. I. J. H. SLOTHOUWER (*Chem. Weekblad*, 1914, 11, 956—958).—Nitration of *p*-fluorotoluene yields a very small proportion of two fluoronitrotoluenes, one having m. p.  $27^{\circ}$  and b. p.  $138-139^{\circ}/83$  mm., and the other b. p.  $134-135^{\circ}/83$  mm. The main product is 3-nitro-*p*-cresol, m. p.  $32^{\circ}$ , proving that the oxidation detaches fluorine from the nucleus.  
A. J. W.

Aldehyde- and Acetone-bisulphites of Organic Bases as Photographic Developers. GUIDO PELLIZZARI (*Ann. Chim. Applicata*, 1914, 2, 129—132).—*p*-Aminophenol in the presence of sulphurous acid forms hydrogen sulphite derivatives with acetone, ethyl acetate, formaldehyde and acetaldehyde, and *p*-methylaminophenol (metol) yields such derivatives with acetone, formaldehyde, and acetaldehyde. Glycine is more acidic than basic and does not form hydrogen sulphite compounds. The compounds formed by acetone with *p*-aminophenol hydrogen sulphite,  $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2\cdot\text{H}_2\text{SO}_3\cdot\text{COMe}_2$ , and with *p*-methylaminophenol hydrogen sulphite,



act as photographic developers in the presence of sodium carbonate, which liberates the amino-compound and the acetone and converts the sulphurous acid into sodium sulphite; the presence of an aldehyde or ketone enhances the reducing power of the developer.  
T. H. P.

Sulphonation of Benzoic Acid. J. MAARSE (*Rec. trav. chim.*, 1914, 33, 207—238).—A determination of the relative proportions of the isomeric sulphobenzoic acids obtained on sulphonating benzoic acid under varying conditions. For the quantitative estimation, the products of sulphonation are converted into the corresponding sulphonyl chlorides by the action of phosphorus pentachloride on the potassium salts, and the solidification points of the resulting mixtures determined. The author has prepared the pure potassium salts of *o*-, *m*-, and *p*-sulphobenzoic acids, and the corresponding acid chlorides and amides. With these substances, solidification curves were obtained for mixtures of the *m*- and *p*-sulphonyl chlorides, and mixtures of the two isomeric ortho-acid chlorides. To detect the presence of small amounts of *o*-sulphobenzoyl dichloride in a mixture of the meta- and para-isomerides, the mixture was submitted to the action of ammonia,

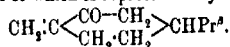
the ortho-compound being thereby converted into the compound,  $C_6H_4 \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{SO}_2 \end{smallmatrix} N \cdot NH_4$ . The liquid was exactly neutralised with hydrochloric acid and filtered, and from the filtrate the "saccharin" was set free by the addition of sulphuric acid and extracted with ether. After evaporating the ether, the residue was dissolved in a few drops of water, a sweet taste at this stage indicating the presence of the ortho-isomeride in the original mixture of acid chlorides. This test is sensitive to considerably less than 1% of the ortho-isomeride in the mixture.

The sulphonations were carried out in the apparatus described by Polak (A., 1911, i, 30), a study being made of the influence of temperature, duration of heating, concentration of the sulphuric acid, relative molecular proportion of sulphuric and benzoic acids, and the presence of a catalyst on the composition of the mixture of sulphobenzoic acids obtained. The presence of *o*-sulphobenzoic acid could only be detected in the one case where mercuric sulphate was used as a catalyst. The main product of the sulphonation was, in all cases, *m*-sulphobenzoic acid to the extent of well over 90%. Variation in temperature, increase in the duration of heating, variation in the concentration of the sulphuric acid (from 100 to 93%), and variations in the molecular proportions of sulphuric and benzoic acids used, had hardly any appreciable effect on the composition of the product. Of the three catalysts tried, potassium sulphate and silver sulphate had little or no influence on the composition of the product, whilst with mercuric sulphate *o*-sulphobenzoic acid was produced to the extent of 0.7% of the total product, as estimated by conversion into salicylic acid and weighing as such after extracting it with chloroform.

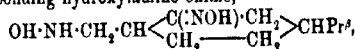
In the latter part of the paper the author discusses the results obtained by various workers on the sulphonation of other benzene derivatives. W. G.

**Calcium *o*-Acetoxybenzoate.** L. VAN ITALLIE and A. P. OLIVIER (*Pharm. Weekblad*, 1914, 51, 1361—1366).—Calcium *o*-acetoxybenzoate is best prepared by passing ammonia into an alcoholic solution containing calcium chloride and *o*-acetoxybenzoic acid in molecular proportions, care being taken to maintain an acid reaction. The salt separates in colourless crystals. A. J. W.

**$\alpha$ -Santolinone, its Formula and Optical Inactivity. Resolution of the Hydroxylamino-oxime Compounds.** L. FRANCESCONI, N. GRANATA and A. MANNA (*Gazzetta*, 1914, 44, ii, 354—356).—The authors discuss the evidence in support of the racemic character of the optically inactive  $\alpha$ -santolinone (this vol., i, 1134), the most probable constitution of which is represented by the formula,



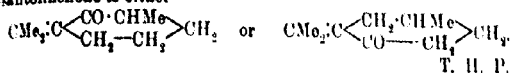
The corresponding hydroxylamino-oxime,



should be capable of existing in a *cis*- and a *trans*-modification for

each form of the ketone, the *d-cis*-compound being enantiomorphous with the *l-cis*-compound, and the *d-trans*- with the *l-trans*-isomeride. As with a number of the ketones of similar structure, it is, however, found that the rupture of the double linking accompanying the formation of the hydroxylamino-oxime can occur only in one way, so that only one pair of enantiomorphous compounds results. Fractionation of the hydroxylamino-oxime *d*-camphorsulphonate gives salts for which the value of  $[\alpha]_D$  in aqueous solution varies between  $-20.35^\circ$  and  $+21.9^\circ$ , the values for the corresponding bases in alcoholic solution ranging from  $-103^\circ$  to  $+16.7^\circ$ .

As will be shown in a subsequent communication, the structure of  $\beta$ -antolinone is either



**Oils of the Coniferae. III. The Leaf and Twig and the Cone Oils of Western Yellow Pine and Sugar Pine.** A. W. SCHORGER (*J. Ind. Eng. Chem.*, 1914, 6, 893—895. Compare this vol., i, 1134, 1172).—The leaves and twigs of western yellow pine (*Pinus ponderosa*) yield from 0.04 to 0.126% of oil having  $D^{20}_D$  0.8718 to 0.8849;  $n^{20}_D$  1.4793 to 1.4838;  $a^{20}_D$   $-15.73^\circ$  to  $-19.39^\circ$ ; acid number, 0.67 to 2.36; ester number, 3.88 to 8.10. The cones of the tree yield 0.063% of oil, having  $D^{20}_D$  0.8757;  $n^{20}_D$  1.4789;  $a^{20}_D$   $-11.48^\circ$ ; acid number, 1.27; ester number, 7.20. The leaves and twigs of the sugar pine, *Pinus lambertiana*, give from 0.45 to 0.12% of oil, having  $D^{20}_D$  0.8676 to 0.8738;  $n^{20}_D$  1.4777 to 1.4795;  $a^{20}_D$   $-11.07^\circ$  to  $-16.50^\circ$ , acid number, 0.68 to 2.38; ester number, 2.22 to 5.91. The cones of this tree yield 0.318% of oil, having  $D^{20}_D$  0.8692;  $n^{20}_D$  1.4771;  $a^{20}_D$   $-23.18^\circ$ ; acid number, 0.63; ester number, 3.75. The percentage composition of the oils was found to be:

	Western yellow pine.		Sugar pine.	
	Leaf and twig oil.	Cone oil.	Leaf and twig oil.	Cone oil.
Furfuraldehyde .....	—	trace	trace	trace
<i>l</i> -Pinene .....	2	6	21	22
<i>l</i> -Camphene .....	—	—	—	21
<i>l</i> - <i>l</i> -Pinene .....	75	60	51	33—40
Dipentene .....	6	12—13	12	4—5
Bornyl ester (as acetate) .....	2	2.5	1.5	1.5
Free alcohol ( <i>l</i> -borneol) .....	7	4	8	3.5
"Green oil" .....	3	3—4	1	—
Sesquiterpene (I) .....	—	—	—	1
Loss, etc. ....	5	10	7	7

W. P. S.

**Gentiacaulin.** MARC BRIDEL (*J. Pharm. Chim.*, 1914, [vii], 10, 329—335).—The author has isolated a large amount of the glucoside gentiacaulin, from *Gentiana acaulis*, by the biochemical method already described (A., 1913, i, 1212), and has made a closer study of its chemical and physical properties. The roots of the plant contain more of the

glucoside than the leafy stem, fresh roots yielding about 2% and the stems about 1%, these values diminishing slightly towards the end of the plant growth. The glucoside, when thoroughly purified, is found to have  $[\alpha]_D - 64.42^\circ$  instead of  $-63.84^\circ$ , as previously given (*loc. cit.*). Dextrose has now been isolated, in addition to xylose, from the products of hydrolysis with boiling 2% sulphuric acid, the proportion of dextrose to xylose being about 55 : 45.

W. G.

**Andrographolide.** K. GORTER (*Rec. trav. chim.*, 1914, 33, 239—243. Compare *ibid.*, 1911, 30, 151).—An attempt to determine whether andrographolide (the bitter principle of *Andrographis paniculata*) contains more than the one double linking already proved to be present (*loc. cit.*). Triacetylandrographolide, dissolved in ether saturated with water, reacts with aluminium amalgam, acetic acid being eliminated and diacetyldeoxyandrographolide,  $C_{20}H_{34}O_7(OAc)_2$ , colourless needles, m. p.  $121^\circ$ , formed. This substance combines only with two atoms of bromine, giving a dibromide, small plates, m. p.  $168^\circ$ , which is still unsaturated since it decolorises potassium permanganate in acid solution. This is confirmed by the fact that diacetyldeoxyandrographolide in acetic acid solution under the influence of platinum black absorbs two molecules of hydrogen, giving diacetyltetrahydroandrographolide,  $C_{20}H_{38}O_7(OAc)_2$ , prisms, m. p.  $90-91^\circ$ . This substance does not decolorise potassium permanganate, and on hydrolysis with alcoholic potassium hydroxide, followed by treatment with dilute sulphuric acid, yields the corresponding lactone, small needles, m. p.  $172-173^\circ$ .

Andrographolide, on boiling with concentrated formic acid for five minutes, followed by the immediate addition of water, yields a compound, small needles, m. p.  $215^\circ$ , which cannot be analysed, owing to the fact that in the combustion tube it decomposes into very difficultly combustible hydrocarbons. This substance cannot be acetylated.

These results show that andrographolide has two double linkings, only one of which can be saturated by bromine, that one of its three hydroxyl groups seems to be tertiary, and that the molecule probably contains two carbocyclic nuclei in addition to the lactonic ring.

W. G.

**Black Pigment in the Skin of an Australian Black.** WILLIAM JOHN YOUNG (*Biochem. J.*, 1914, 8, 460—462).—The pigment was prepared by dissolving the skin of the Australian Black in 5% potassium hydroxide solution and then acidifying with hydrochloric acid, when the melanin was precipitated as a dark brown powder. It was purified by repeated precipitation from its alkaline solution. It contains C 60.12, H 6.70, N 11.89, Fe 0.21%, and some sulphur (unestimated). A solution of the pigment in 5% potassium hydroxide or in concentrated sulphuric acid absorbs all the rays in the violet, the blue and, in part, the green of the spectrum to a wave-length of about  $515 \mu$ . Beyond this point there is slight blurring of the green and orange, whilst the red is practically unaffected.

H. W. B.

**Transformation of Glutamic Acid into *l*-Pyrrolidonecarboxylic Acid in Aqueous Solution.** FREDERICK WILLIAM FOREMAN (*Biochem. J.*, 1914, 8, 481—493. Compare Abderhalden and Kautsch, *A.*, 1910, i, 768; 1912, i, 492).—When an aqueous solution of glutamic acid is heated above 80°, a certain proportion of it is converted into *l*-pyrrolidonecarboxylic acid, and the same change occurs with an acid salt of glutamic acid, but to a smaller extent. Mineral acids exert an inhibitory action to an extent proportional to their strength and to the amount present. The presence of more than 8% of sulphuric acid or about 3% of hydrochloric acid inhibit the change altogether.

The reverse change, namely of *l*-pyrrolidonecarboxylic acid into glutamic acid, occurs on boiling with concentrated hydrochloric acid.

It appears that the occurrence of pyrrolidonecarboxylic acid among the products of protein hydrolysis is often due to this secondary change.

H. W. B.

**Diketotriazines.** J. BOUGAULT (*Compt. rend.*, 1914, 159, 631—633. Compare this vol., i, 1004).—Diketotriazines can be prepared quite well by the action of cold dilute alkali on the semicarbazones of the corresponding  $\alpha$ -ketonic acids, the yield being better than on heating owing to the elimination of a secondary action, but the process requires several months under these conditions. With sodium hypobromite, diketotriazines give bromo-acid amides and nitrogen is evolved. Thus 4:6-diketo-3-benzyltriazine yields *aa*-dibromo- $\beta$ -phenylpropionamide,  $\text{CH}_2\text{Ph}\cdot\text{CBr}_2\cdot\text{CO}\cdot\text{NH}_2$ , m. p. 138°, which is reduced by zinc in acetic acid to phenylpropionamide, m. p. 105°. 4:6-Diketo-3-phenylethyltriazine similarly yields *aa*-dibromo- $\gamma$ -phenylbutyramide,  $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{CBr}_2\cdot\text{CO}\cdot\text{NH}_2$ , m. p. 139°, yielding on reduction phenylbutyramide. This behaviour on oxidation with sodium hypobromite is a further proof of the constitution of the diketotriazines.

W. G.

**Gelatinisation of Pectin in Solutions of the Alkalis and the Alkaline Earths.** DOROTHY HAYNES (*Biochem. J.*, 1914, 8, 553—583).—The rate of gelatinisation of pectin is not determined by the rate of diffusion or by the rate of adsorption of the alkali or alkaline earths producing gelatinisation, but by the rate of a chemical reaction involving the replacement of hydrogen by potassium, barium, strontium, or calcium and hydroxyl ions. That a reaction of this kind takes place is supported by the facts that it can be expressed by a velocity equation involving the concentrations of the reacting substances, and that the constitution deduced for compounds of the alkalis and alkaline earths with pectin is strictly analogous to that of the corresponding compounds of the mono- and di-saccharides. Similar molecular compounds with salts are probably also formed. Gelatinised pectin forms solid solutions with the alkaline earths which may be compared with the solid solutions of lime and sucrose.

H. W. B.

**Activation of Trypsinogen.** HORACE MIDDLETON VERNON (*Biochem. J.*, 1914, 8, 494—529. Compare this vol., i, 214).—The author describes experiments from the results of which he draws the

conclusion that in the activation of trypsinogen by enterokinase, the trypsin liberated in the earlier stages by the direct action of the enterokinase gradually sets free an enzyme (termed *deuterase*, to indicate that it acts secondarily to enterokinase) from a precursor, and that this deuterase is mainly responsible for the later stages of the activation process. It is found that the rate of activation of the trypsinogen during the last half of the process (when deuterase is acting) may be one thousand times more rapid than the initial rate, and it is independent of the amount of enterokinase used.

Deuterase has a temperature coefficient of 1.00 to 1.22 and is further distinguished from enterokinase by the fact that the former is relatively much more retarded in its action by glycerol, and the latter by Witte's peptone.

There is no relationship between the amounts of deuterase and trypsin present in pancreatic extracts prepared from various animals. A glycerol extract of monkey's pancreas contained only a fourth as much trypsin as a glycerol extract of pig's pancreas, but two-thirds as much deuterase. Some extracts of ox pancreas did not seem to contain any deuterase, but this was shown to be due to the masking action of an anti-substance. Deuterase is extremely unstable, except in the presence of glycerol, and therefore, aqueous pancreatic extracts have relatively little activating power; freshly activated pancreatic juice was observed to lose most of its activating power in two hours at 37°, owing probably to destruction of the deuterase by trypsin. Both trypsin and trypsinogen appear to exist in various degrees of stability.

The activating power of deuterase may be nearly doubled by the addition of small quantities of intestinal extract which themselves do not possess any appreciable activating power. Deuterase is not, however, regarded as a co-enzyme of enterokinase. H. W. R.

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## Physiological Chemistry.

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Determination of the Composition of the Different Proteins of Ox and Horse Serum by the Method of Van Slyke. PENCIVAL HARTLEY (*Biochem. J.*, 1914, 8, 541—552).—The author has separated the proteins of ox and horse serum, and estimated the ammonia-, melanin-, cystine-, arginine-, histidine-, lysine-, and residual amino- and non-amino-nitrogen present in each compound by van Slyke's method (*A.*, 1911, ii, 944). The conspicuous differences existing between serum-albumin and serum-globulin with regard to their content of cystine, diamino-acids (particularly lysine, melanin and ammonia, are advanced by the author as additional evidence controverting Moll's statement of a transformation of serum-albumin into serum-globulin occurring in warmed blood serum (compare Bywaters and Tasker, *A.*, 1913, i, 1399). On the

other hand, the similarity of the figures obtained for the various globulins supports the views of Chick (this vol., i, 1145) regarding the close relationship existing between euglobulin and  $\psi$ -globulin.

H. W. B.

**Influence of Excessive Water Ingestion on Protein Metabolism.** JOHN BOYD ORR (*Biochem. J.*, 1914, 8, 530—540. Compare Fowler and Hawk, A., 1910, ii, 625).—A series of experiments carried out on men shows that the excessive ingestion of water produces an increased excretion of urinary nitrogen, due chiefly to an increase in the elimination of ammonia and urea. The action is not, however, to be regarded as a mere flushing out of waste products from the system, because it is found that the most marked rise in the urinary nitrogen after water drinking occurs on a low protein diet, whilst when the subject is on an excessively high protein diet, where a large amount of nitrogenous end-products would be present in the system, the smallest rise occurs in the total urinary nitrogen. In the latter case, although during the period of excessive water ingestion the total urinary nitrogen remains almost stationary, the absolute amount of urea, and the percentage of the total nitrogen excreted as urea, both increase. This result, which is obtained in all the experiments, shows that the main effect of excessive water drinking is a stimulation of the catabolic processes of metabolism. Since, on returning to a normal water consumption, a retention of nitrogen is observed, the period of excessive water ingestion is also attended by a stimulation of the anabolic phases of protein metabolism.

The appearance of creatine instead of creatinine in the urine during the period of excessive water drinking, as recorded by Fowler and Hawk (*loc. cit.*), was not observed. A decrease in the faecal nitrogen, indicating a more complete utilisation of the protein of the food, is another of the beneficial effects accompanying copious water drinking.

H. W. B.

**Physiology of Reproduction in the Domestic Fowl. IX. Effect of Corpus Luteum Substance on Ovulation in the Fowl.**

RAYMOND PEARL and FRANK M. SURFACE (*J. Biol. Chem.*, 1914, 19, 263—278).—The desiccated fat-free substance of the corpus luteum of the cow, when injected in suspension, in proper dosage, into an actively laying fowl immediately inhibits ovulation. The duration of this effect varies with different birds from a few days to two to three weeks. After the bird begins ovulating again, the laying goes on unimpaired. The same effect is produced by the injection of extracts of the luteal substance, either intravenously or intra-abdominally. The active substance which produces the inhibition is inactivated by boiling.

H. W. B.



## Chemistry of Vegetable Physiology and Agriculture

**Significance of Certain Substances for Plant Growth.** W. E. BOTTOMLEY (*Ann. Bot.*, 1914, 28, 531-540).—Peat which was subjected to the action of certain aerobic soil organisms at 26°, and after being sterilised, mixed with nine parts of soil and kept for seventeen days at 26°, induced a considerable fixation of nitrogen, amounting with two different soils to 77 and 54 mg. per 100 grams of soil.

Further experiments with various plants showed that aqueous extracts of the bacterised peat (1 part of peat to 200 of water) supplied all the plant food required, and that seedlings of *Prunella malacoides* (in loam, leaf-mould, and sand) grew to twice the size when treated twice with an aqueous extract of 0.18 gram of the peat.

Stimulating effects were obtained by employing the residue of an alcoholic extract of peat, by the phosphotungstic acid precipitate from an aqueous extract of the same residue, and finally by the silver fraction, corresponding with Funk's "vitamin" fraction. The last substance added to a complete nutritive solution, at the rate of 0.35 per million, increased the growth of excised wheat seedlings grown for fifty days 59%. The plants showed a continuous growth, whilst those without the peat substance increased 14.7% in sixteen days, and then lost in weight, the final loss being 10.9%. It is suggested that during germination substances are formed which enable the embryo to utilise the food present in the seed, and that this substance can be wholly or partly replaced by the substance obtained from peat.

N. H. J. M.

**Injurious Root Secretions.** D. PRIANISCHNIKOV (*Rev. gen. Bot.*, 1914, 25, 563-582).—The results of experiments in which etiolated wheat plants were grown successively in the same distilled water showed no reduction in the yield; under these conditions, no substance toxic to wheat seems to be secreted by the roots of wheat. In sand and soil-culture experiments it was found, however, that the yields of subsequent crops were considerably reduced, according to the plants grown, not only when the same plant was grown two or three times in succession, but with different plants. The reduction in yield was much greater when the roots of the first plant were left in than when they were removed.

Oats grown in an extract of black soil gave a very small yield, whilst normal growth was obtained when the extract was filtered through charcoal. When the extract was distilled, and both the distillate and the residue employed as culture solutions, the former produced a normal growth and the latter a much smaller yield; the difference was still more marked when the distillation was conducted under reduced pressure.

The conclusion is drawn that roots contain a substance which is

toxic both to the same and to other plants. It is suggested that the cause of the reduced yield of a second growth may be the increased alkalinity, which would be greater when the first crop is removed during early periods of growth, and varies according to the plant grown. On the other hand, alkalinity is not removed by charcoal, which in some cases raised the yield to its original amount.

The experiments referred to form part of a research by Péritzeine (*Ann. Inst. agron. Moscou*, 1913, No. 4; in Russian).

N. H. J. M.

**Origin of Vanillin in Soils. Vanillin in Wheat and in the Water in which Wheat Seedlings have Grown.** M. X. SULLIVAN (*J. Ind. Eng. Chem.*, 1914, 6, 919-921).—Since vanillin, or a closely related parent substance, appears to be fairly widely distributed in the vegetable kingdom, the author has determined whether or not vanillin can be detected in wheat, as a type of field crop, and in the water in which wheat has grown. Un-germinated wheat was found to contain about three parts per million of vanillin; the quantity increases slightly during the early growth of the plant, and the substance can pass from the plant to the medium of growth either directly or, more probably, as a result of cell sloughing and disintegration. Treatment of the ground seeds with acids increases the yield of vanillin, this being due, apparently, to the hydrolysis of the parent substance; the latter is regarded as being coniferin. Vanillin is also found in rotten oak wood, pineapple pulp, and lawn grasses. Its presence in wood and various forms of vegetation would lead to the conclusion that the vanillin found in soil has its origin in vegetable debris and, to a minor extent, in direct excretion or cell sloughing by growing plants.

W. P. S.

**Analyses of Two Echinacea Roots.** F. W. HEYL and J. F. STALEY (*Amer. J. Pharm.*, 1914, 86, 450-455).—The following results were obtained on the analysis of the roots of two species of the genus *Brauneria* (*Echinacea*) obtained from Kansas and Missouri: *B. angustifolia*: moisture, 10.90%; starch, none; pentosans, 15.6; "crude fibre," 24.77%; protein, 6.54%; ash, 7.76%; inulin, 5.9%; resin, 1.84%; sucrose, 6.92%; reducing sugars, 3.65%. *B. purpurea*: moisture, 10.18%; starch, none; pentosans, 15.6%; "crude fibre," 29.65%; protein, 5.31%; ash, 6.93%; inulin (not estimated); resin, 2.00%; sucrose, 3.40%; reducing sugars, 3.41%. *B. angustifolia* also yielded 0.04% of an amber-coloured, volatile oil, but did not contain any alkaloid sufficiently basic to be extracted by the ordinary methods; this does not exclude the possibility of the presence of choline and allied substances.

W. P. S.

**Plant Chemistry.** P. Q. KEEGAN (*Chem. News*, 1914, 110, 211-212).—Qualitative analyses of various plants. In *Parnassia pilustris* a moderate amount of mucilage, a tannoid, and a catechol

tannin were found. *Pinguicula vulgaris* contains a good deal of mucilage, sucrose, and tannoid, but no tannin. Nitrates were not found in either plant. The golden saxifrage was found to produce much mucilage, with some gum, a little nitrate, some sucrose, a little tannin, but no tannoid. Holly-leaved barberry resembles ivy; both contain caffetannin and a tannoid, probably quercetinagenin (the former containing more caffetannin and the latter more tannoid), and the aqueous extracts of the leaves show several reactions in common. *Mimulus luteus* contains nitrates and about 1% of caffetannin, but no tannoid. An examination of both leaves and roots of wild geranium showed that the leaves (in July) contained a little nitrate, much sucrose, considerable gallotannin and tannoid, but very little catechol-tannin; the roots contained no nitrates and no sucrose, but considerable amounts of starch and calcium oxalate.

The relation of assimilation and deassimilatory processes in plants to the reaction of the protoplasm is discussed.

N. H. J. M.

**Urease Content of Certain Indian Seeds.** HAROLD EDWARD ANNETT (*Biochem. J.*, 1914, 8, 449—452).—Urease has been detected in the following seeds: sword bean (*Canavalia ensiformis*), kharai, kalai (*Dolichos biflora*), *Urana lobata*, and six varieties of soy bean. The sword bean contains, weight for weight, several times as much urease as the soja bean, and may possibly be substituted for it in the estimation of urea (compare Plimmer and Skellern, this vol., ii, 306).

H. W. B.

**Investigation of the Diastase of Alfalfa [Lucerne] and the Effect of Rapid Curing on the Food Value of Alfalfa.** R. C. SHUKY (*J. Ind. Eng. Chem.*, 1914, 6, 910—919).—The diastatic activity of lucerne (*Medicago sativa*) is greater in the morning or after a period of darkness than after exposure to light. Much more diastase is present in the plants during the summer than in the spring and autumn, and the younger plants contain the larger quantity. Drying in a moist atmosphere at 50° decreases the diastatic activity, but it is considerably increased when the material is dried in a current of air with gradual increase of temperature. Light and weathering in the field tend to destroy the diastase, and the effect of rain during the curing is very injurious. Highly diastatic lucernes generally contain more water-soluble constituents than specimens low in diastase, but the water-soluble substances cannot be increased above a certain limit (about 40%). The loss of digestible constituents during handling and curing may vary from 20% under favourable conditions to as much as 50% under adverse weather conditions. Curing by artificial heat gives a hay of better colour, odour, and flavour than can be produced by other means, and the cost of artificial drying is estimated to be less than that due to losses sustained during curing in the field.

W. P. S.

**Chemical Changes during Silage Formation.** RAY E. NEIDIG (*J. Amer. Chem. Soc.*, 1914, 36, 2401—2413).—In earlier work (Dox and Neidig, A., 1913, i, 236), a study has been made of the acids and alcohols contained in maize silage. An account is now given of an investigation of the changes occurring during silage formation in silos of three different types: (1) a hollow clay tile silo; (2) a wooden silo; and (3) a concrete silo. The following changes were observed, but no differences were noticed which could be attributed to the materials of which the silos were constructed. Non-reducing sugar was rapidly changed to reducing sugar, and the amount of the latter subsequently decreased. The quantity of volatile acids and lactic acid increased daily. Small quantities of alcohol were produced. Carbon dioxide was formed with considerable rapidity after the silos had been filled, and free oxygen disappeared from the silos after the second or third day. The maximum temperature reached in any of the silos was 32.5°. E. G.

**Acid Mineral Soils.** G. DAIKUHARA (*Bull. Imp. Centr. Agric. Exper. Stat. Japan*, 1914, 2, 1—40).—Results of pot experiments in which barley was manured with potassium chloride, in addition to ammonium sulphate and disodium hydrogen phosphate, showed that whilst satisfactory results were obtained in two clay soils, the effect of the potassium salt in a sandy granite soil was to reduce the yield to almost nothing. Addition of calcium carbonate along with the manures resulted in a very great increase over the unmanured pots. The soil, which contained only a small amount of humus, was found to give a strongly acid reaction, due to the absorption by the soil colloids of aluminium or iron compounds. In presence of potassium chloride, soluble acid aluminium or iron compounds are formed.

The examination of a considerable number of Japanese and Korean soils showed that three-fourths of them were acid, and that in the case of more than half of these the acidity was due to absorbed aluminium or iron compounds. Soils from mesozoic formations are the most frequently acid, then tertiary, palaeozoic, and diluvial soils.

The examination of twenty specimens of kaolin showed that thirteen were acid, four neutral, and three alkaline. The acid kaolins behave towards neutral salt solutions in the same way as acid soils, whilst the others, after treatment with dilute acids and washing, become acid and acquire the properties of acid kaolins; similar results were obtained by subjecting granite and other alkaline rocks to the action of aqueous carbon dioxide for some weeks.

The acidity of soils is increased by treatment with dilute acids.

The filtrates from the soils treated with potassium chloride solution give with ammonia a precipitate consisting mainly of aluminium hydroxide, the amount of which corresponds with the acidity of the soil, and the amount of  $N/10$ -alkali used in the titration.

Soil acidity can be detected by moistening 5 grams of the soil

in a test-tube with a 10% solution of potassium nitrite, and suspending a strip of potassium iodide-starch paper in the tube by means of a cotton-wool plug. Acidity due to colloid absorption can be detected by treating the soil in a watch-glass with potassium chloride solution and testing with litmus paper.

To estimate the acidity, the air-dried soil (100 grams) is shaken for an hour with 250 c.c. of normal potassium chloride solution. One hundred and twenty-five c.c. are then boiled to remove the carbon dioxide, and titrated with  $N/10$ -sodium hydroxide. The treatment is repeated as long as the extract is acid, 150 c.c. of fresh potassium chloride being added each time. N. H. J. M.

**An Acid Soil in Assam.** A. A. MEGGITT (*Mom. Dept. Agr., India Chem. Ser.*, 1914, 3, 235-269).—The soil is very old alluvium and is a light loam in good physical condition, containing an adequate amount of potassium, and a moderate amount of humus, whilst it is deficient in phosphoric acid, and especially so in calcium carbonate (0.02%). The soil contains an organic acid which is toxic to some plants in solutions containing 30 per million. In the case of some plants, however, the substance is not only non-toxic, but is beneficial in concentrations which are injurious to other plants. The toxicity is more or less completely overcome by adding a complete nutritive solution, or by neutralising with lime.

In practice it has been found that whilst some plants, such as *Phaseolus mungo*, will grow on the soil and give a moderate crop, others fail to get beyond the stage of seedlings unless considerable amounts of lime are added. For neutralisation, the soil requires 880-1350 parts of lime per million.

The results of a large number of plot experiments with various manures, with and without lime, showed that in absence of lime most of the plots failed altogether, the exceptions being those which received basic manures (sodium and potassium carbonates and basic slag), and some which received superphosphate.

The fact that superphosphate, in absence of lime, enabled the plants to grow is attributed to its action in stimulating root development, resulting in extra-cellular root oxidation and the destruction of the toxic substance. The effect of superphosphate, which is very much less than that of lime, is increased by addition of sodium nitrate. N. H. J. M.

## General and Physical Chemistry.

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**Index of Refraction and Density of Gases.** A. OCCHIALINI (*Nuovo Cim.*, 1914, [vi], 8, ii, 123—155).—Magri (1904) has shown that, at pressures up to 200 atmospheres, the refractive indices of air give values for the Lorenz and Lorentz formula which are appreciably more constant than those calculated by means of Brude's or Gladstone and Dale's expression. The author has extended Magri's observations by measuring the indices of refraction and the corresponding specific gravities of nitrogen and oxygen at various pressures up to 200 atmospheres and of carbon dioxide up to the saturation point at 21°. The maximum percentage variations of the value of the Lorenz and Lorentz formula are 0.05, 0.3, and 0.2 for nitrogen, oxygen, and carbon dioxide respectively, such variations lying within the limits of experimental error. For Brude's and Gladstone and Dale's formulae the corresponding percentage variations are respectively 2.3 and 8.5 for nitrogen, 2.7 and 0.8 for oxygen, and 1.4 and 0.5 for carbon dioxide. The value of  $(n^2 - 1)/(n^2 + 2)D$  is  $1997 \times 10^{-7}$ ,  $1815 \times 10^{-7}$ , and  $3003 \times 10^{-7}$  for the three gases respectively.

These results show that the value calculated, by the Lorenz and Lorentz formula, for the index of refraction of a gas at any particular density is more accurate than that obtainable by direct measurement.

T. II. P.

**Fluorescence of Iodine Vapour Excited by Ultra-violet Light.** J. C. McLENNAN (*Proc. Roy. Soc.*, 1914, [A], 91, 23—29).—The fluorescence spectrum of iodine vapour, which was described in a previous paper (A., 1913, ii, 435), has been further investigated. Observations on the effect of temperature show that the spectrum is excited at all temperatures between that of the room and 1000°. In contrast with this, it is found that the resonance spectrum, excited by the yellow and green lines, is only obtained at comparatively low temperatures. No trace of this spectrum was observed at 326°.

The fluorescence spectrum is called forth when the wave-length of the exciting light falls between the limits  $\lambda$  2100 and  $\lambda$  1800. On the other hand, the resonance spectra cannot be obtained when the iodine vapour is illuminated by light from a mercury arc of wave-length less than that of the green line  $\lambda$  5460.

The investigation of a number of iodine compounds has shown that iodoform and mercuric iodide give a fluorescence spectrum which contains the seven well-marked bands of the iodine fluorescence spectrum between  $\lambda$  3315 and  $\lambda$  3175. In addition to the iodine lines, the mercuric iodide spectrum contains a number of specific bands which are absent from the iodine spectrum.

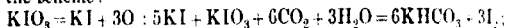
With potassium iodide, a fluorescence spectrum is obtained which does not show any of the iodine bands. It consists of two sets of

unequally spaced fine lines in the regions between  $\lambda 4047$  and  $\lambda 3340$  and between  $\lambda 3075$  and  $\lambda 2940$ . H. M. D.

**Theories of Rotational Optical Activity.** G. H. LIVESY (Phil. Mag., 1914, [vi], 28, 756—757).—A reply to Brubat (this vol., ii, 695), in which the author maintains that Drude's theory has been shown, both directly and indirectly, to be incapable of explaining the known facts in regard to optical rotatory power.

H. M. D.

**Photolysis of Potassium Iodate.** J. HOWARD MATHEWS and HARRY A. CURTIS (J. Physical Chem., 1914, 18, 641—652).—The action of light of short wave-length has been investigated in the decomposition of solutions of potassium iodate. Solutions of 0.1*N*-potassium iodate were placed in a quartz flask and kept at a temperature of 30° by allowing a stream of water at this temperature to flow over them. Light from a mercury-vapour lamp was allowed to fall on the flask, when iodine was liberated. The amount of iodine liberated was estimated from time to time by titration with a 0.001*N*-solution of potassium thiosulphate. The following results were obtained: (1) When the photolysis is carried out in the presence of air, the rate of the reaction slowly decreases with time. (2) Iodine is not liberated when the solution is kept saturated with oxygen in an atmosphere of oxygen. (3) Carbon dioxide greatly increases the rate of photolysis; and (4) the rate of photolysis of potassium iodate in a solution kept saturated with carbon dioxide is linear when the amount of iodine liberated is small compared with the total amount present in the iodate. It is therefore not possible in such circumstances to determine the order of the reaction. It is suggested that the photolysis occurs according to the scheme:



the liberation of oxygen has been experimentally proved. Light accelerates the reaction between potassium iodate, potassium iodide and carbon dioxide, but the reaction is very complex in the presence of light, and has not been quantitatively investigated. A lecture experiment to demonstrate the photochemical activity of light of short wave-lengths is described. To a solution of 0.1 gram of potassium iodate in 500 c.c. of water, 2 c.c. of a 1% solution of potassium iodide and 2 c.c. of starch solution are added. One-half of the solution is placed in a quartz flask, and the residue in a glass flask. The flasks are placed at equal distances from a quartz mercury lamp, and in a few seconds the solution in the quartz flask turns blue, whilst the other remains quite colourless.

J. F. S.

**Radioactivity of Some Colorado Springs.** HERMAN SCHLESER (J. Physical Chem., 1914, 18, 662—666).—The activity of the gases evolved by the water of a number of springs has been measured by means of a Mache-Meyer fontactometer with an ionisation chamber of 15 litres. The readings are taken from two to three minutes

after the introduction of the gas. The results are expressed in Mache units, and vary from 0.21 to 31.2 units. The equivalents in radium are calculated, and they vary from  $1.2 \times 10^{-10}$  gram to  $265 \times 10^{-10}$  gram. The gases from three of the springs were tested for thorium emanation, but the results were negative. Mention is made of the sinter deposit, round a group of radioactive springs investigated by Headden (A., 1905, ii, 2); this consists almost entirely of barium sulphate, which contains  $14.8 \times 10^{-10}$  gram of radium per gram; this corresponds with nearly 0.5% of uranium in the natural mineral.

J. F. S.

**Ionisation Potential of Mercury Vapour.** F. H. NEWMAN (*Phil. Mag.*, 1914, [vi], 28, 753—756).—Experiments were made to determine the smallest potential difference through which an electron must fall before it is able to ionise a molecule of mercury by collision. Working at  $79^\circ$ , at which the vapour pressure of mercury is about 0.1 mm., the value obtained was 5.0 volts. This agrees closely with the 4.9 volts obtained by Franck and Hertz (this vol., ii, 515).

H. M. D.

**Concentration Cells in Ionised Gases.** W. H. JENKINSON (*Phil. Mag.*, 1914, [vi], 28, 685—692).—Assuming that the passage of electricity from metal to air is a phenomenon which may be treated as thermodynamically reversible, the potential difference at the surface of contact should be given by the formula

$$\pi = RT(2r-1)/\epsilon \cdot \log P/p,$$

in which  $p$  is the ionic pressure of either kind of electricity in the air and  $P$  is the equivalent of the "solution pressure" for the metal, the ions of which are transferred. If two wires are in contact with regions of air, in which the ionic pressures are  $p_0$  and  $p_1$ , then on the assumption that  $P$  is unaltered by the ionising agency, the two wires should form a concentration cell, the *E.M.F.* of which should be given by  $E = RT(2r-1)/\epsilon \cdot \log p_0/p_1$ .

A cell of this kind was constructed by connecting up two carefully insulated copper wires to a Dolezalek electrometer and exposing one of the wires to the action of X-rays or of the rays emitted by radium. In all cases, a deflexion was gradually set up, which ultimately reached a steady value, and reversed its sign when the action of the ionising agent was transferred from one electrode to the other. The unprotected electrode was always found to be positive with respect to the shielded electrode. This indicates that the positive ion must be the controlling agent in the production of the difference of potential at the metal air surface. The results suggest, in fact, that the negative ions take no part in the transfer of electricity across the surface.

It is suggested that the presence of an occluded layer of gas in the metal surface is an essential feature in the production of this difference of potential, and that  $P$  represents the ionic pressure in this occluded layer. According to this view, the transference of electricity at the surface is effected by means of positively charged air-ions.

H. M. D.



**Distribution of the Molecules of a Gas in a Field of Force, with Applications to the Theory of Electrons.** O. W. RICHARDSON (*Phil. Mag.*, 1914, [vi], 28, 633—647).—The question of the distribution of the molecules of a perfect gas in equilibrium in a field of force is discussed from the point of view of the quantum theory. The theory is also applied to thermo-electric phenomena and to the thermionic emission of electrons. H. M. D.

**Electrical Resistance of Pure Metals, etc. IX. Resistance of Mercury, Tin, Cadmium, Constantan, and Manganin down to Temperatures obtainable with Liquid Hydrogen and with Liquid Helium at its Boiling Point.** H. KAMERLINGH ONNES and G. HOLST (*Proc. K. Akad. Wetensch. Amsterdam*, 1914, 17, 508—513. Compare this vol., ii, 163).—Further measurements of the resistance of solid mercury have been made at temperatures between  $-268.9^{\circ}$  and the melting point ( $-38.93^{\circ}$ ). The ratio of the resistances of liquid and solid mercury at the melting point is about 5. Data are also recorded showing the influence of temperature on the resistance of tin and cadmium between  $165^{\circ}$  and  $-268.9^{\circ}$ , of iron and copper between  $-183.7^{\circ}$  and  $-272.0^{\circ}$ , of constantan between  $-182.3^{\circ}$  and  $-258.8^{\circ}$ , of manganin between  $16.5^{\circ}$  and  $-271.5^{\circ}$ , and of gold between  $-182.3^{\circ}$  and  $-258.9^{\circ}$ .

The resistance of manganin varies with the temperature in a linear manner from the lowest oxygen temperatures down to helium temperatures. The temperature coefficient of constantan, which is extremely small down to oxygen temperatures, increases considerably in the region of hydrogen temperatures. Between  $16^{\circ}$  and  $20^{\circ}$  (absolute) the relation between the resistance and the temperature is linear in character. It seems probable that gold may also be used for the measurement of temperatures below  $-200^{\circ}$ . H. M. D.

**Conductivity of Certain Organic Acids in Absolute Ethyl Alcohol at  $15^{\circ}$ ,  $25^{\circ}$ , and  $35^{\circ}$ .** E. P. WIGHTMAN, J. B. WHITE, and HARRY C. JONES (*J. Amer. Chem. Soc.*, 1914, 36, 2243—2259).—In continuation of earlier work on the conductivity of organic acids (White and Jones, A., 1910, ii, 13, 821; Wightman and Jones, A., 1911, ii, 689; 1912, ii, 1035; Smith and Jones, A., 1913, ii, 747), measurements have been made of the conductivity of malonic, *o*- and *p*-chlorobenzoic, *p*-bromobenzoic, *o*- and *p*-nitrobenzoic, 3:4-dinitrobenzoic, 3:4-dihydroxybenzoic, and tetrachlorophthalic acids in ethyl alcohol at  $15^{\circ}$ ,  $25^{\circ}$ , and  $35^{\circ}$ .

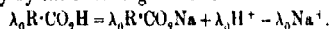
The temperature-coefficients of conductivity are very large, ranging from 15% to 50%. The conductivity often shows a rapid increase with increase in dilution, but *o*-chloro- and *p*-nitrobenzoic acids behave in the opposite manner. The conductivities of organic acids in alcohol are exceedingly small as compared with those of the same acids in aqueous solution, being in some cases several hundred times smaller; this fact cannot at present be satisfactorily explained. E. G.

**Sensitive Criterion of the Precision and of Constant Errors in the Conductance Data of Weak Electrolytes, the Determination of the Molar Conductance of Organic Electrolytes at Zero Concentration, and a Study of the Correction for the Specific Conductance of the Conductivity of Water.** C. G. DEANIX (*J. Amer. Chem. Soc.*, 1914, 36, 2268—2283).—The conductivity of a weak electrolyte at infinite dilution can be calculated from the expression

$$\lambda_0 = \lambda\lambda_1(c\lambda - c_1\lambda_1)(c\lambda^2 - c_1\lambda_1^2),$$

where  $\lambda$  and  $\lambda_1$  represent the molar conductivities at the concentrations  $c$  and  $c_1$ . Kendall's work on the conductivity of acetic acid in aqueous solution (T., 1912, 101, 1283) indicates that acetic acid very nearly obeys the ideal mass law in this form, and the latter may be used in the calculation of the molar conductivity of acetic acid at zero concentration, the value of which is termed the "calculated"  $\lambda_0$ .

The molar conductivity at zero concentration can be determined independently by the following "salt method":



A comparison of the "calculated"  $\lambda_0$  for weak electrolytes, such as acetic acid, with that obtained for the same acid by the salt method affords a means of detecting constant errors in conductivity data. Kendall's data for acetic acid give the value 398 for the "calculated"  $\lambda_0$ , whilst the salt method gives 388; it is therefore evident that, assuming the mobility of the hydrogen ion is 347 for such weak electrolytes, some constant error is present in these data.

On assuming the ideal mass law to hold for transition electrolytes, and determining the values for "calculated"  $\lambda_0$  at different concentrations, a regularity was obtained in the increase of these values with decreasing concentration until a maximum constant value was reached at a concentration below which no deviations could be detected. This maximum constant value for the molar conductivity of the electrolyte should obviously be identical with the value obtained by the salt method, and this is shown to be the case with the organic acids studied by Kendall (*loc. cit.*).

The value 347 for the mobility of the hydrogen ion at 25° as given by Kendall and others is probably accurate, at least for the transition electrolytes.

It is shown that the "calculated"  $\lambda_0$  can be employed to determine whether a correction for the specific conductivity of the water used in the dilution of the organic acid should be applied to the conductivity data, the method being to calculate the values for "calculated"  $\lambda_0$  for the corrected and the uncorrected data, and compare them with the value of  $\lambda_0$  obtained by the salt method. Consideration of Kendall's results shows that no water correction should be applied to his data on transition electrolytes when the specific conductivity of the water is less than  $0.9 \times 10^{-6}$ , since his uncorrected data give "calculated"  $\lambda_0$  values which agree with those obtained by the salt method with an accuracy greater than 0.1% in the dilute solutions.

E. G.

**The Least Energy Required to Start a Gaseous Explosion.** W. M. THORNTON (*Phil. Mag.*, 1914, [vi], 28, 734-738. Compare this vol., ii, 524).—A comparison has been made of the minimum energies of the igniting break-sparks of continuous and alternating current with those of condenser discharge between platinum poles. The observations were made with gases containing about 10% of methane or coal-gas in admixture with air, and electrodes of iron, nickel, and copper were employed in the comparison.

At voltages of 100 to 200, the least igniting energy varies from 0.02 to 0.15 joule in the case of continuous current, whilst the corresponding numbers for alternating current vary from 0.15 to 0.5 joule. The energy-voltage curves seem to indicate that the duration of any least-igniting break-spark is inversely proportional to its energy. The ignition is dependent on the nature of the gaseous mixture and of the incandescent matter which is projected into it from the poles. In continuous current ignition, the material of the poles is the important factor, whereas the nature of the gas is decisive in the case of ignition by alternating current discharge. The facts suggest that the ignition brought about by low-frequency alternating discharge is thermal in origin, and that some other factor operates in the case of ignition by continuous current discharge.

H. M. D.

**Ignition of Gases by Condenser Discharge Sparks.** W. M. THORNTON (*Proc. Roy. Soc.*, 1914, [A], 91, 17-22. Compare this vol., ii, 524).—Experiments have been made to determine the least energy required for the ignition of explosive gas mixtures by condenser sparks between platinum poles at a potential difference of 100 volts. The observations were made with methane, ethane, propane, butane, carbon monoxide, hydrogen sulphide, and hydrogen mixed with air in varying proportions. The results are shown in the form of curves in which the capacity of the least igniting condenser discharge is plotted as a function of the composition of the gas mixture. These curves are not continuous, but so far as those mixtures are concerned which contain a smaller proportion of air than the most easily ignited mixture, they are characterised by one or more breaks or steps which indicate a sudden change in the case of ignition when the gas mixture reaches a certain composition.

In the case of methane no ignition could be obtained when the mixture contained less than 6.25% of this gas. From 6.25 to 10.5% the energy of the least igniting spark remained constant at 6.5 microfarads, but at 11.5% the necessary energy suddenly increased until 16 microfarads were required for ignition. The mixture corresponding with the formation of carbon dioxide is thus passed through without any marked change; the mixture corresponding with carbon monoxide is at 12%. At 13-13.5% of methane, 40 microfarads were necessary for ignition, and in mixtures containing a larger proportion of methane, ignition could not be brought about.

The stepped ignition curve has been found in all the gases employed in the experiments with the exception of butane, and in this case the ignition curve was not examined except in a preliminary manner.

The author suggests that the cause of the change in the resistance to ignition is probably to be found in the circumstance that when an atom of combustible gas is surrounded by molecules, with one or more of which it is eventually to combine, the difficulty of choice of any single partner is increased by the simultaneous attraction of the others, and more energy must be supplied to set up a movement sufficiently violent for any pair to be forced into "contact." In carbon monoxide the critical mixtures correspond with 3, 6, and 9 molecules of carbon monoxide for one molecule of oxygen. In methane the steps correspond with 3 and 4 molecules of oxygen to one molecule of methane, and in hydrogen the critical ratios of hydrogen molecules to oxygen atoms are 1, 2, 3, and 6.

H. M. D.

**Conductivity of Extremely Dilute Acid and Alkali Solutions.** H. H. PAINE and G. T. R. EVANS (*Proc. Camb. Phil. Soc.*, 1914, 18, 1—13. Compare Whetham and Paine, A., 1908, ii, 802).

From measurements of the electrical conductivity of very dilute solutions of sulphuric acid, it is found that the relation between the conductivity and the concentration of the acid corresponds with a straight line provided that the concentration is not less than about  $0.8 \times 10^{-5}$  gram-equivalent per litre. For smaller quantities of acid, the observed conductivity is greater than that which would correspond with the straight line relation and the deviation between the two values increases as the concentration falls. The conductivity of the water employed in the experiments, in which the above limiting value of the acid concentration was obtained, was  $0.36 \times 10^{-6}$  mho.

It is shown that the observations can be accounted for in a satisfactory manner if it is assumed that the residual conductivity of the distilled water is mainly due to the presence of a carbonate, and experiments made with a very dilute solution of ammonium carbonate, to which gradually increasing quantities of sulphuric acid were added, support this view.

According to Kohlrausch's data, the conductivity-concentration curve for dilute solutions of potassium hydroxide deviates from the straight line at a higher concentration than that which is found for the sulphuric acid curve, but this is what would be expected on the assumption that the impurity is ammonium carbonate.

H. M. D.

**The Silver Voltmeter. III. The Solvent Properties of Silver Nitrate Solutions.** T. MARTIN LOWRY (*Proc. Roy. Soc.*, 1914, [A], 91, 53—71. Compare Smith and Mather, *Phil. Trans.*, 1908, [A], 207, 545; Smith and Lowry, *ibid.*, 581).—Experiments have been made to determine the solubility of silver chloride, bromide,

iodide, and sulphide in concentrated aqueous solutions of silver nitrate, and also of silver chloride in concentrated solutions of sodium chloride and hydrochloric acid.

The measurements were made according to two different methods, which may be illustrated by reference to the solubility of silver chloride in silver nitrate solutions. Those at constant temperature were made by a gravimetric method, in which the weight of silver chloride precipitated on the addition of a measured quantity of sodium chloride was determined, and the quantity of dissolved salt obtained by difference. The influence of temperature on the solvent capacity of a solution of fixed concentration was ascertained by adding a measured quantity of sodium chloride under such conditions that a clear solution was obtained. The tube containing the hot solution was provided with a thermometer and stirrer, and was placed in a hot water-bath, the temperature of which was allowed to fall slowly. At a certain point the solution became opalescent in consequence of the separation of silver chloride, and this temperature was determined for a series of solutions.

*Silver Chloride* [with F. HAWKES, J. F. POTTS, and R. G. PARKER].—The data for 20° show that the quantity of silver chloride which is dissolved by 100 grams of silver nitrate increases from 0.0294 gram for the solution  $\text{AgNO}_3 : \text{H}_2\text{O} = 1 : 2$  up to 0.1372 gram for the solution 2 : 1. The quantity of silver chloride dissolved by a given solution increases with the temperature, and the temperature effect becomes more marked as the concentration of the nitrate in the solution increases. The curve obtained by plotting the dissolved silver chloride as a function of the temperature is convex to the temperature axis in the case of 1:2, concave for 2:1, and practically a straight line for the solution 1:1.

The data for the solubility in chloride solutions refer to 15, 20, and 28% solutions of sodium chloride, and a 20% solution of hydrochloric acid. The solubility increases in all cases with rise of temperature.

*Silver Bromide, Iodide, and Sulphide* [with R. G. PARKER].—The data for silver bromide show that the solubility of this in concentrated silver nitrate solutions is approximately three to four times as great as that of the chloride. The solubility of silver iodide in silver nitrate solutions has already been determined by Hellwig (A., 1900, ii, 723), but some observations relative to the influence of temperature on the solubility in a 25% solution are recorded. In this solution the solubility reaches a maximum at about 60°. If the solution saturated at this temperature is heated to 100°, silver iodide is precipitated; if allowed to cool, the solution becomes cloudy at about 50°, and white needles of  $\text{AgI} \cdot \text{AgNO}_3$  are deposited. If these are left in contact with the mother liquor at the ordinary temperature, they are transformed into the double salt  $\text{AgI} \cdot 2\text{AgNO}_3$ . Roughly speaking, the iodide is about thirty times more soluble than the bromide, and about 100 times more soluble than the chloride.

Silver sulphide is less soluble in nitrate solutions than the chloride. The black sulphide represents the stable solid phase in

contact with dilute nitrate solutions, but this is transformed into the yellow double salt  $\text{Ag}_2\text{S}, \text{AgNO}_3$  in contact with more concentrated solutions.

The quantity of silver sulphide retained per 100 grams of silver nitrate increases with the temperature, and at  $100^\circ$  amounts to 0.06 gram for a 40.8% solution, and to 0.243 gram for a solution containing 74% of silver nitrate.

H. M. D.

**Current Potentials of Electrolyte Solutions.** H. R. KRUVT (*Proc. K. Akad. Wetensch. Amsterdam*, 1914, 17, 615—622).—Measurements have been made of the differences of potential which result from the movement of dilute solutions of electrolytes through a capillary tube. In the apparatus used by the author, this capillary tube formed a connexion between two vessels, in which were suspended two silver electrodes covered with a layer of silver chloride. The solution was forced through the capillary at a constant speed, and the difference of potential between the electrodes measured by the Poggendorff method.

From experiments in which the solution was made to pass through the capillary at different rates, it was found that the difference of potential is directly proportional to the driving pressure.

In order to ascertain the influence of the cation, observations were made with solutions of potassium, barium, and aluminium chlorides. The curves obtained by plotting the potential difference against the concentration show that the addition of extremely small quantities of these electrolytes to conductivity water reduces the potential difference to a very marked extent. The influence increases very considerably with the valency of the cation, and the addition of  $0.8 \times 10^{-6}$  mol. of aluminium chloride per litre is sufficient to reduce the potential difference from 0.35 volt to zero. Further addition of aluminium chloride changes the sign of the potential, which, after reaching a maximum of 0.13 volt, diminishes gradually as the concentration of the aluminium chloride is further increased.

In the case of potassium and barium chlorides no change in the sign of the potential difference was observed, although the concentration was increased to  $10^{-3}$  mol. per litre for potassium chloride and to  $40 \times 10^{-3}$  mol. per litre for barium chloride.

The difference of potential observed with conductivity water is attributed to the selective adsorption of  $\text{OH}'$  ions by the glass, and the reduction of this on the addition of the electrolytes, to selective adsorption of the respective cations.

H. M. D.

**Electric Charge and Limit Value of Colloids.** H. R. KRUVT (*Proc. K. Akad. Wetensch. Amsterdam*, 1914, 17, 623—629).—The data obtained in measurements of the capillary electric potential for solutions of potassium chloride and barium chloride (compare preceding abstract) show the existence of a close connexion between this phenomenon and the coagulation of colloidal particles by these electrolytes.

H. M. D.

**Electrolytic Endosmose.** HORACE G. BYERS and CARL H. WALTER (*J. Amer. Chem. Soc.*, 1914, 36, 2284—2291).—Experiments

are described which were carried out with a simple tripartite cell, consisting of two battery cups, set about  $\frac{1}{2}$  inch apart in a battery jar. In each cup a platinum electrode was placed, and an intermittent siphon, so that any rise in the level of the liquid would cause an overflow into a suitable graduated vessel. The whole apparatus was filled with the solution to be examined, and the level of the liquid in the battery jar was maintained during the experiment by adding more of the solution from a reservoir through a dropping siphon. Experiments were made with solutions of potassium permanganate, potassium perchlorate, sodium chloride, copper sulphate, copper nitrate, sodium sulphate, borax, potassium alum, and ferric chloride. Some experiments were conducted with a cell with six compartments.

The results show that endosmose is capable of producing a flow of electrolyte in the direction of the current, in the opposite direction, or in both directions simultaneously. In some cases the electrolyte flows away from both electrodes, and also may flow more rapidly from one than to the other; in each case the volume in the middle compartment of a tripartite cell is increased. In a cell with six compartments the change in volume is not confined to the anode and cathode compartments, but varies in the other compartments in an apparently erratic manner. When clay membranes are used, the endosmose is complicated by stenolysis. E. G.

**Alternating Current Electrolysis.** JNANENDRA CHANDRA GHOSH (*J. Amer. Chem. Soc.*, 1914, 36, 2333—2346).—Le Blanc and Schick (A., 1904, ii, 230) have expressed the view that electrolysis by means of an alternating current depends on the formation of a complex ion, whilst Brochet and Petit (A., 1904, ii, 229; 1905, ii, 672) consider that the presence of complex ions is not necessary, but that the general condition for the formation of a new compound is that the ion on reaching the electrode has had time to part with its charge before reversal produces the ion of opposite charge at the same electrode. In connexion with this question, the author has thought that as the electrode potential is due to the electrical double layer at the surface of separation between the electrode and electrolyte, a study of the amount and direction of variation of electrode potential might possibly elucidate the nature of the changes at the electrode surface.

When an alternating current is passed through cadmium in cadmium sulphate solution or through copper in copper sulphate solution, no variation in the electrode potential is produced. These results indicate that only when there is such a change as would alter definitely the chemical nature of the electrical double layer is its effect noticeable by measurements of the electrode potentials.

Experiments were also carried out to determine the changes in the electrode potentials in cells containing two platinum electrodes immersed in various electrolytes. On passing the alternating current, small variations in the *E.M.F.* were observed in all cases, but these were greatest in the case of acids, the amount of variation in this case being from 0.2 to 0.4 volt. It is evident, there-

fore, that on a polished platinum surface the chemical process is not reversible, but that the ion has time to part with its charge and form other more stable substances. Variations in *E.M.F.* were also observed when mercury electrodes were employed, but these were smaller than in the case of platinum and of a somewhat different nature. When electrodes of platinum-black were used, the variation in electrode potential almost disappeared, and in no case exceeded 0.015 volt, whence it is evident that there is not any appreciable consumption of energy at the electrode surface.

The effect of alternating currents on the single electrode potentials of combinations which have an *E.M.F.* of their own was investigated. In the case of cells containing an electrode, consisting of a metal surrounded by its insoluble salts, such as the cell  $\text{Zn} \text{ ZnCl}_2 \text{--HgCl--Hg}$ , the effect of impressing an alternating current is to increase the amount of polarisation at the mercury electrode, and necessarily to increase the amount of the polarising current which the cell furnishes of itself. Several other types of cell were also studied.

E. G.

**Thermal Expansion of Solutions of Gelatin in Water.** **AUTHUR A. SCOTT** (*J. Physical Chem.*, 1914, 18, 677—680).—The coefficients of cubical expansion of 2%, 6%, and 10% solutions of gelatin in water have been determined at temperatures from 0° to 10°. The solutions were sterilised with a little mercuric chloride, and filled into a glass helix made from 150 cm. of tubing of uniform bore. One end of the tube was sealed, and a meniscus produced at the other surface of the jelly by pouring in about 1 cm. of petroleum. The apparatus was then placed in a thermostat, and the position of the meniscus read by means of a microscope at every degree change in temperature. The coefficient of expansion of a 2% jelly is increasingly negative to 3°, when it becomes less negative up to 7°, where it is positive; 6% and 10% jellies have positive coefficients over the whole range 0—10°, which steadily increase as the temperature rises.

J. F. S.

**Vapour Pressures in Ternary Systems.** **W. P. JORISSEN** (*Chem. Weekblad*, 1914, 11, 964—972).—A critical summary of work previously published.

A. J. W.

**Cryoscopic Constant of Nitrobenzene.** **J. BÖSEKEN and J. A. L. M. C. VAN DER EERDEN** (*Rec. trav. chim.*, 1914, 33, 301—316).—The authors have determined the cryoscopic constant of nitrobenzene used as solvent in molecular-weight determinations in the case of aromatic hydrocarbons, their haloid and nitro-derivatives, phenols and some derivatives, aromatic acids and some derivatives, aliphatic alcohols and some derivatives, aliphatic acids, aldehydes, ketones, acid anhydrides, and amines and some derivatives. The nitrobenzene is purified by drying the commercial sample over calcium chloride, and distilling it when required; the determinations are made out of contact with moist air. The m. p. of the nitrobenzene, thus prepared, is 5.60°, the value of the cryoscopic constant being



between 69 and 70. This solvent can be used for substances which do not contain either a carboxyl or a hydroxyl group. In nitrobenzene, acids are more associated than alcohols and phenols; the acids are associated at low concentrations, the association changing but little with the concentration. Alcohols show an association which increases rapidly with the concentration but diminishes as the molecular weight of the alcohol increases, and is greatest for primary alcohols and least for tertiary alcohols of the same molecular weight. The carbonyl and the hydroxyl groups have each for itself an associating action much less than that of the carboxyl group. In these respects nitrobenzene is analogous to benzene and naphthalene as a solvent, the association, however, being generally less pronounced in the former than in the last two solvents.

W. G.

**Free Energy of Iodine Compounds.** GILBERT N. LEWIS and MERLE RANDALL (*J. Amer. Chem. Soc.*, 1914, 36, 2259—2268).—In continuation of the study of free energy of chemical substances (Lewis, A., 1913, ii, 112; Lewis and Randall, this vol., ii, 802), the free energies of iodine and its compounds have been calculated from existing data. The following values (in calories) of the free energy of formation ( $\Delta F^\circ_{298}$ ) have been obtained: iodine, I (solid, 0; I (liquid), 460; I<sub>2</sub> (gas), 4640; I (gas), 16965; I<sub>2</sub> (in aqueous solution), 3926; hydrogen iodide, HI (gas), 310; iodide ion, I<sup>-</sup>, -12304; tri-iodide ion, I<sub>3</sub><sup>-</sup>, -12216; hypoiodous acid, HIO (in aqueous solution), -23300; iodate ion, IO<sub>3</sub><sup>-</sup>, -32270. E. G.

**The Values of the Critical Quantities in Case of Association.** J. J. VAN LAAR (*Proc. K. Akad. Wetensch. Amsterdam*, 1914, 17, 598—606).—A criticism of the conclusions arrived at by van der Waals (this vol., ii, 342, 538). It is shown that in the case of an associated substance, there is no linear relation between the association factor and the quantities  $T_k p_k$  and  $s = RT_k p_{k1}$ . Such a relation does not hold even when association is not accompanied by a change of volume, and the deviations from it may be much greater when the association is attended by volume change.

H. M. D.

**Temperature-coefficients of the Free Surface Energy of Liquids between -80° and 1650°. VII. The Specific Surface Energy of the Molten Haloids of the Alkali Metals.** F. H. JAEGER (*Proc. K. Akad. Wetensch. Amsterdam*, 1914, 17, 555—571. Compare this vol., ii, 805, 806).—The method, described in a previous paper, has been applied to the measurement of the surface tension of the molten fluorides and chlorides of lithium, sodium, potassium, rubidium, and caesium, and the bromides and iodides of sodium, potassium, rubidium, and caesium. Although in most cases, the surface energy is a linear function of the temperature, the connexion between these quantities is for certain salts more accurately given by the quadratic formula:

$$\chi_t = a + b(t - t_s) + c(t - t_s)^2,$$

in which the constant  $a$  represents the surface energy at the melting point  $t_m$ . In general, the value of the constant  $b$  is smaller for molten salts than for organic substances, but exceptions are met with in lithium, sodium, and rubidium fluorides.

The data show further that the temperature coefficient  $b$  for the haloids of the same alkali metal decreases in all cases with increasing atomic weight of the halogen. At a given temperature the surface energy values for the series of salts formed by the same halogen with the series of alkali metals, decreases with increasing atomic weight of the alkali metal. In the same way, the surface energy of the haloids of one and the same alkali metal decreases with increasing atomic weight of the halogen if the comparison is made at a fixed temperature.

H. M. D.

**Temperature-coefficients of the Free Surface Energy of Liquids at Temperatures between  $-80^\circ$  and  $1650^\circ$ . VIII. The Specific Surface Energy of Some Salts of the Alkali Metals.** F. M. JAEGER (*Proc. K. Akad. Wetensch. Amsterdam*, 1914, 17, 571–584. Compare preceding abstract).—The surface tension of molten oxygen salts of the alkali metals has been measured at different temperatures. Data are recorded for the sulphates and nitrates of lithium, sodium, potassium, rubidium, and caesium, the metaborates of lithium, sodium, and potassium, and the molybdates, tungstates, and metaphosphates of sodium and potassium. As in the case of the alkali metal haloids, the temperature coefficient is constant for a number of the oxy-salts, but for others a quadratic formula is necessary to express the relation between the surface energy and the temperature.

At a given temperature the surface energy of a series of alkali metal salts of the same acid decreases with increasing atomic weight of the alkali metal. An exception to this rule is presented by lithium nitrate, in that its surface energy is less than that of sodium nitrate.

H. M. D.

**Adsorption and Stabilisation.** J. C. BLEUCHER and E. F. FARNAU (*J. Physical Chem.*, 1914, 18, 629–640).—The various theories which have been put forward to explain the process of dyeing are discussed, and it is shown that the adsorption theory coupled with Bancroft's theory of stabilisation of the dye, to explain the process of dyeing from colourless solutions, is most nearly in accord with facts. This theory (this vol., ii, 250) states that the fibre stabilises the otherwise unstable substance which it has adsorbed. Thus blue cupric hydroxide when adsorbed by wool is not converted into oxide by heating at  $100^\circ$ . A number of other instances are quoted in the paper, including the stabilisation of blue cobalt hydroxide by cobalt sulphate and by nickel hydroxide, and of the red acid of Congo-red by aluminium hydroxide. A number of experiments are described on the stabilisation of cupric hydroxide. A number of tubes containing cupric hydroxide suspended in water are treated with small quantities of manganese sulphate, zinc sulphate, nickel sulphate, cobalt chloride, aluminium sulphate, chromium

sulphate, magnesium chloride, and mercuric chloride, and the mixtures heated at  $100^{\circ}$ . The cupric hydroxide turns black very rapidly when there has been no addition made, but with the exception of mercuric chloride all the other substances retard the formation of cupric oxide to such an extent that no blackening occurs after heating for ten minutes. The fact that silk is not dyed by a solution of picric acid in benzene is considered, and the conclusion reached that the apparent irreversibility in dyeing silk from benzene solutions of picric acid is probably a question of tautomerism as well as of slowness of attainment of equilibrium.

J. F. S.

**Measurements of the Capillarity of Liquid Hydrogen.** H. KAMERLINGH ONNES and H. A. KUYPERA (*Proc. K. Akad. Wetensch. Amsterdam*, 1914, 17, 528—532).—Measurements of the surface tension of liquid hydrogen have been made by the method of capillary rise. The corrected rise is a linear function of the temperature for the interval examined. According to the linear formula, the capillary rise should vanish at  $35.98^{\circ}$  (abs.). Since the critical temperature is  $31.11^{\circ}$  (abs.), it is evident that the formula loses its validity before the critical temperature is reached.

The surface tension decreases from 3.182 dynes per cm. at  $14.6^{\circ}$  to 2.126 at  $20.40^{\circ}$  (abs.). The data yield 1.464 for the value of the temperature-coefficient of the molecular surface energy, which is much lower than the average value for so-called normal substances. It would seem that this coefficient decreases with fall in the critical temperature.

According to the theory underlying Einstein's formula (*Ann. Physik*, 1911, [iv], 34, 165), it would seem that the radius of molecular action for hydrogen is larger than for substances such as benzene.

H. M. D.

**Molecular Kinetic Elements of the Vapours of Isomeric Compounds.** A. POCHETTINO (*Nuovo Cim.*, 1914, [vi], 8, ii, 5—36).—The author has determined, by Stefan's method, the coefficients of diffusion,  $D$ , into air of the vapours of (1) the series of esters studied by Meyer (A., 1878, 368), Meyer and Schumann (A., 1881, 504), and Winkelmann (A., 1885, 10; 1886, 11), and (2) various other groups of structural and position isomerides. The reduction of the values of  $D$  to a common temperature was effected by means of Sutherland's formula:

$$D_2/D_1 = (T_2/T_1)^{1.2} \cdot (1 + c/T_1)/(1 + c/T_2),$$

in which  $c$  represents a constant characteristic of the pair of gases under consideration; better concordance is obtained by this formula than by the relation  $D_1/D_2 = T_1^2/T_2^2$ , deduced from the old kinetic theory of diffusion. From the values thus obtained, those of  $L$ , the mean path of the molecules, of  $\sigma$ , the diameter of the sphere of molecular action, and of  $Q$ , the sum of the sectional areas of the spheres of action of the molecules in unit volume, have been calculated.

As might be foreseen, increase of the number of atoms in the

molecules of homologous compounds is accompanied by diminution in the mean path of the separate molecules and by increase in the diameter of the sphere of action. In the case of isomeric compounds with normal, and therefore equal, vapour densities, the molecules of the vapour differ in the diameters of their spheres of action, iso-compounds giving lower values than those of normal structure. This observation is related to the fact that, according to van't Hoff's hypothesis, the centres of the carbon atoms are nearer with iso-compounds than with normal ones. In the following series of isomeric compounds, the values of  $\sigma$  are in order of diminishing magnitude, whilst those of the propinquity of the carbon atoms, as judged from the steric formula, are in order of ascending magnitude: butyl alcohol, isobutyl alcohol, ethyl ether, trimethylcarbinol; propylbenzene, isopropylbenzene, mesitylene; butylamine, isobutylamine, diethylamine; benzyl chloride, *o*-, *m*-, *p*-chlorotoluenes; ethylbenzene, *o*-, *m*-, *p*-xylenes. With isomeric compounds of the formula  $C_nH_{2n}O_2$ , leaving aside the acids,  $\sigma$  is smallest for that isomeride in which the position of the group  $COO$  is such that the two atomic complexes attached to the two carbon atoms are most nearly similar; the association of the acids in the liquid state seems to influence the values of  $l$  and  $\sigma$ .

The increase in the value of  $\sigma$  produced by addition of a  $CH_2$  group varies with the molecular structure of the original compound. With the acids  $C_nH_{2n}O_2$  its mean value is  $1.12 \times 10^{-8}$ , and with the isomeric esters  $0.56 \times 10^{-8}$ .

Since the value of the coefficient  $b$  of van der Waals' equation is related to that of  $\sigma$  according to the equation  $b = 4\pi N\sigma^3/6$ ,  $b$  and  $\sigma$  should increase together in series of isomeric compounds, and this is found to hold in general, although exceptions do occur. Further, according to the Mossotti-Clausius law, the fractional volume,  $v$ , actually occupied by the molecules of a gas is connected with the dielectric constant  $K$ , and the index of refraction,  $n$ , for  $\lambda = \lambda_0$ , by the relation  $v = (K-1)/(K+2) = (n^2-1)/3$ ; this method of comparing the molecular dimensions agrees with the values of  $\sigma$  in the case of ethyl formate and methyl acetate, but not in that of ethyl acetate and methyl propionate.

The values of  $l$  given by the diffusion method were compared, for a number of the compounds investigated, with those derived from measurements of the coefficients of internal friction of the vapours. The agreement between the two series of values is not good, but the variation observed in passing from a compound to an isomeric one is in the same direction, and approximately of the same magnitude in the two series.

Measurements of the thermal conductivity of the vapours of a number of the compounds show that, in a group of isomeric compounds, the values of the conductivity and of  $l$  increase together.

T. H. P.

**Interpretation of the Indications of Atomic Structure Presented by Crystals when Interposed in the Path of X-Rays.**  
WILLIAM BARLOW (*Proc. Roy. Soc.*, 1914, [A], 91, 1-16).—A

theoretical paper in which it is shown that the nature of the spacing of the parallel planes of atomic centres, as indicated by the behaviour of crystals towards X-rays, is more or less ambiguous. The arguments put forward show that an atomic system, arranged according to any one of the three space-lattices possessing cubic symmetry, may be subjected to a certain kind of deformation, sufficient in amount to alter profoundly the nature of the arrangement, without any appreciable evidence of this deformation being presented by the X-ray data. So far as geometrical possibilities are concerned, a similar method of modification can be applied to all kinds of space-lattice arrangements of atoms of whatever symmetry, so as to produce from them point-systems which would have an effect on X-rays practically indistinguishable from that produced by the unmodified space-lattice arrangements. Such modifications of the space-lattice or space-lattices leave the system of crystal symmetry unaltered, but lower the class. The fact that hemihedry is in so many cases exhibited by the crystals of simple compounds, may be regarded as an indication that the actual arrangement of the atoms is of the less symmetrical kind.

In the case of a crystal of sodium chloride, the need for some modification of the model described by W. L. Bragg (*ibid.*, 1914, A, 88, 428) is suggested by the fact that the arrangement does not lend itself to a distribution of the centres of the molecules in harmony with the crystal symmetry. If, however, the arrangement of the atoms is one derived from the cubic space-lattice by appropriate deformations, the difficulty presented by the crystal symmetry is avoided. The suggested modification is not only in harmony with the results of X-ray observations, but is in better agreement with the following facts: (1) that the centres of the molecules are arranged according to cubic symmetry; (2) that the symmetry is not holohedral, but hemihedral, like that of the actual crystals; (3) that stable equilibrium is indicated by the relation of each centre to the centres surrounding it.

H. M. D.

**Rhythmical Precipitation of Ferrous Ferricyanide and Ferrous Hydroxide in Jelly.** HENRY JERMAIN MAUDE CREIGHTON (*J. Amer. Chem. Soc.*, 1914, 36, 2357—2360).—Liesegang (A., 1906, ii, 273; 1907, ii, 533; this vol., ii, 631) and others have investigated the rhythmical precipitation of silver chromate and other salts in gelatin. Similar phenomena have now been observed with ferrous ferricyanide and ferrous hydroxide.

The experiments were carried out in a glass tube, 2 cm. in diameter, the ends of which were bent upwards at right angles. The tubes were filled with 10% solution of agar-agar containing, in one case, small quantities of potassium ferrocyanide and sodium chloride, and, in the other case, small quantities of phenolphthalein and sodium chloride. When the jelly had solidified, the vertical arms of the tube were filled with dilute sodium chloride solution, and an iron electrode, made from a clean wire nail, was placed in the liquid in each arm. An electric current was then passed through the jelly. In the case of the tube containing potassium

ferrocyanide, blue layers or disks of ferrous ferricyanide were formed at intervals, the intervening spaces containing colourless jelly. The rate of production of these disks and the distance between them were noted. In the case of the tube containing phenolphthalein, green disks of ferrous hydroxide appeared, separated from one another by pink jelly. E. G.

**Distribution of Colloidal Arsenious Sulphide Between the Two Liquid Phases in the System Water, Ether, Alcohol.** HARRY P. COLLINS (*J. Physical Chem.*, 1914, 18, 681-694).—The binodal curve and tie lines for the system water, ethyl ether, ethyl alcohol previously determined by Bonner (A., 1911, ii, 26) were redetermined, and the specific gravity of solutions of known composition on the binodal curve were also determined. The method employed here is the same as that previously adopted (*loc. cit.*). A graph has been constructed which allows of the composition of any one pair of solutions in equilibrium being found by determining its specific gravity. A method of allowing for the effect of colloidal dissolved arsenious sulphide on the densities has been worked out and tested experimentally. It is shown that as regards the system water, ether, alcohol, the compositions at equilibrium are not affected by the presence of colloidal arsenic sulphide. Bifid solutions of arsenic sulphide containing alcohol and ether are more transparent, and are less readily coagulated by salts than aqueous solutions, and the amounts of different salts required to coagulate them do not vary as much as in the case of water sols. Solutions containing alcohol, ether, water, and arsenic sulphide undergo change on keeping; the amount of arsenic found in the strata after coagulation with acid increases, and the proportion of colloid going into the upper layer on distribution decreases. Quantitative measurements of the distribution of the arsenic sulphide between the two phases show that when one and the same colloid preparation is used, and the measurements are carried out under the same conditions, the ratio of distribution varies continuously with the composition of the phases, and that, other things being equal, the fraction of the arsenic sulphide going into the upper layer decreases with increase in the concentration of the sulphide. J. F. S.

**Equilibria in Quaternary Systems. X. Quaternary Mixtures with two Liquid Strata, and Quaternary Alloys of Nickel-Copper-Gold-Silver.** N. PARRAVANO (*Gazzetta*, 1914, 44, n. 279-349. Compare A., 1913, ii, 763).—Six different types of quaternary systems are subjected to theoretical treatment, which does not admit of satisfactory abstraction. From the percentage variation exhibited by any one component, it is found possible to calculate the quantities of liquid and solid constituting a given quaternary mixture, and hence those of the separate liquids and solids composing the liquid and solid mixtures, for any moment during the solidification. In conjunction with P. DE CESARIS, MAZZETTI, and U. PERRET, the author has investigated the

ternary and quaternary systems of Ni-Cu-Au-Ag, the results obtained with the quaternary alloys being borne out by those given by micrographical examination. T. H. P.

**Equilibrium in the System Mercuric Iodide and Aniline**  
J. N. PEARCE and E. J. FRY (*J. Physical Chem.*, 1914, 18, 667—676).

—The system mercuric iodide and aniline has been studied between the temperatures of  $-11.48^{\circ}$  and  $199.1^{\circ}$ . The portion of the curve below the melting point of aniline,  $-8^{\circ}$ , is the freezing-point curve of the solution in equilibrium with solid aniline; at  $-11.48^{\circ}$ , solid aniline and the compound  $\text{HgI}_2 \cdot 2\text{NH}_2\text{Ph}$  separate out together as a eutectic mixture. The solubility of mercuric iodide in aniline has been determined at a series of temperatures between  $-6.5^{\circ}$  and  $191.1^{\circ}$  when the following values, expressed in grams of mercuric iodide in 100 grams of aniline, were obtained:  $-6.5^{\circ}$ , 23.35 grams;  $+0.4^{\circ}$ , 28.69 grams;  $17.8^{\circ}$ , 42.85 grams;  $21.1^{\circ}$ , 47.55 grams;  $25.5^{\circ}$ , 55.47 grams;  $30.1^{\circ}$ , 62.05 grams;  $36.2^{\circ}$ , 73.80 grams;  $42.9^{\circ}$ , 86.19 grams;  $48.8^{\circ}$ , 128.1 grams;  $63.6^{\circ}$ , 163.8 grams;  $70.82^{\circ}$ , 184.1 grams;  $76.2^{\circ}$ , 201.6 grams;  $95.9^{\circ}$ , 246.7 grams;  $115.7^{\circ}$ , 281.8 grams;  $137.2^{\circ}$ , 285.2 grams;  $181.1^{\circ}$ , 297.9 grams; and  $199.1^{\circ}$ , 863.2 grams. The solubility of the iodide increases rapidly up to  $46.8^{\circ}$ , and is in equilibrium with a white, crystalline solid,  $\text{HgI}_2 \cdot 2\text{NH}_2\text{Ph}$ , which melts at  $58.6^{\circ}$ . The temperature  $46.8^{\circ}$  is a quadruple point, where  $\text{HgI}_2$ ,  $\text{HgI}_2 \cdot 2\text{NH}_2\text{Ph}$ , solution and vapour are in equilibrium. At  $108^{\circ}$ , the solid phase is the red variety of mercuric iodide, but as the yellow iodide is formed, and a second quadruple point exists, at about this temperature a greenish-yellow solid begins to be formed, which has the composition  $\text{HgI}_2 \cdot \text{NH}_2\text{Ph}$ . The various saturated solutions were analysed by dissolving weighed quantities in acetic acid solution of potassium iodide, and then precipitating the mercury with hydrogen sulphide, filtering on a Gooch crucible, washing with water and absolute alcohol, drying and removing the sulphur, and finally heating at  $70^{\circ}$  until of constant weight. It is shown that mercury sulphide is decidedly volatile at temperatures above  $70^{\circ}$ ; for example, 0.6879 gram lost 0.0194 gram when kept at  $80^{\circ}$  for three hours, whilst at  $110^{\circ}$  2.3076 grams lost 0.55 gram in two hours. J. F. S.

**Influence of Some Substituents in the Benzene Nucleus on the Velocity of Reaction in the Synthesis of Sulphones**

S. C. J. OLIVIER (*Rec. trav. chim.*, 1914, 33, 244—251).—Using a method, slightly modified, already described for determining the velocity of reaction of *p*-bromobenzenesulphonyl chloride with benzene and its mono-substituted derivatives in the presence of aluminium chloride (this vol. i, 818), the author has determined the effect of replacing the bromine in *p*-bromobenzenesulphonyl chloride by other substituents on the velocity of its reaction with benzene in the presence of aluminium chloride. Using 1 mol. of aluminium chloride for each mol. of acid chloride, the reactions are all unimolecular, the constant of the reaction being proportional to the concentration of the aluminium chloride introduced.

The substituent groups,  $\text{CH}_3$ , H, I, Br, Cl,  $\text{NO}_2$  (in the meta position), arranged here in the order of diminishing velocity constant, have the same proportionate influence whether introduced into the nucleus of the acid chloride or of the benzene, except that the influence is in general greater in the latter case. W. G.

**Catalytic Action.** J. BORSEKEN (*Proc. K. Akad. Wetensch. Amsterdam*, 1914, 17, 546--554).—In the main, this is a re-statement of the author's views on catalysis, recorded in a previous paper (this vol. ii, 554). An ideal catalyst is defined as a substance which reacts reciprocally with one of the substances which are to be rendered active in such a manner that the thermodynamic potential and chemical resistance simultaneously approximate to zero. H. M. D.

## Inorganic Chemistry.

**Production of Neon and Helium by the Electrical Discharge.** J. NORMAN COLLIE, HUBERT S. PATTERSON, and IRVINE MASSON (*Proc. Roy. Soc.*, 1914, [A], 91, 30-45).—A detailed account is given of the experiments already published (T., 1913, 103, 419; P., 1913, 29, 233, 271), and also of the results obtained in new experiments. For as yet unexplained reasons, many of these experiments have yielded negative results.

The apparatus used was partly of the transference type, in which the gas to be examined was transferred from one vessel to another by means of a tube standing over mercury, and partly of the non-transference type, in which the testing apparatus could be placed in connexion with the experimental tube by opening a tap.

The hydrogen was removed by means of heated copper oxide or by explosion with oxygen; in the latter case, the oxygen was removed by sodium-potassium alloy or by charcoal. The residue was examined in capillary tubes so fine that the mercury, once admitted, could only be withdrawn by strongly heating the tubes.

The least quantity of neon detectable corresponds with that in a few cubic millimetres of air. If this were due to leakage, then since the ratio of argon to neon in air is 700 : 1, the argon should have been readily detected and also probably some nitrogen.

The main results obtained in positive experiments are the following: *A.* Using discharge tubes of various kinds and electrodes of palladium, copper, lead, thallium, lithium, sodium, and potassium, helium or neon was obtained, and in many experiments both gases were detected. *B.* Experiments in which platinum, thallium, uranium, potassium fluoride, chloride and iodide, rubidium chloride and calcium carbonate were subjected to bombardment by cathode rays, gave helium and in some cases neon. *C.* According to earlier



observations on the mercury arc, considerable quantities of helium and neon were obtained in this form of discharge; but according to more recent experiments it would seem that this may be due to diffusion of air through the silica walls of the discharge tube. Further work on the electrodeless discharge has also shown that the conditions under which helium is produced are as yet not known with certainty.

It is to be noticed that, especially in experiments falling under A and C, considerable quantities of hydrogen disappear during the passage of the discharge.

In all experiments, great precautions were taken to ensure the purity of the gases used. Although control experiments seem to eliminate the possibility of air leakage, special experiments were made in which traces of air were admitted into the apparatus. After running the discharge tube for some time under these conditions, it was found that nitrogen was absorbed by the mercury, but that argon was left behind which could be readily detected in the examination tube, and formed a very sensitive test for a leak. A further quantity of argon could be obtained by heating the electrodes. This test for argon is therefore extremely delicate as a means of detecting air leakage.

The negative results obtained by Strutt (this vol., ii, 201) are attributed (1) to the use of too large a charcoal bulb which may have resulted in the absorption of the neon produced, (2) to the use of relatively wide capillary examining tubes, (3) to possible absorption by "splashed" metal, (4) to the type of discharge which has a considerable influence on the yield.

In a former paper it has been shown that the positive results are not due to permeation of the glass. That they are not due to occlusion has been shown by dissolving or melting the glass and the electrodes, when no helium or neon was obtained.

The authors draw no definite conclusion from the observations, but they consider that the trend of the results is towards conditions which, if true, would be of obvious importance. H. M. D.

**The Ternary Systems Potassium {Potassium Hydroxide-Phosphoric Acid-Water and Ammonia-Phosphoric Acid-Water.** E. G. PARKER (*J. Physical Chem.*, 1914, 18, 653-661).—The object of the work was to ascertain whether a stable compound of potassium, ammonia, and phosphoric acid could be produced with the purpose of thus obtaining a concentrated chemical fertilizer. The two above-mentioned ternary systems were therefore examined. Solutions of orthophosphoric acid from 1.4 to 9.77 mols. per 1000 grams of solution were shaken at 25° with potassium hydroxide of 8.56-40.12 mols. per 1000 grams of solution in equilibrium with the existing solid phase was set up. The liquid and solid phases were then analysed, and equilibrium isotherms plotted. It is shown that the solid phases stable in contact with the solutions are:  $\text{KH}_2\text{PO}_4 \cdot \text{H}_3\text{PO}_4$ ;  $\text{KH}_2\text{PO}_4$ ;  $\text{KPO}_3$ ;  $\text{K}_3\text{PO}_4 \cdot 3\text{H}_2\text{O}$ ; and  $\text{KOH} \cdot 2\text{H}_2\text{O}$ . Similar experiments were carried out with ammonia 2.77-14.08 mols. per 1000 grams of solution.

and phosphoric acid 6.09—0.41 mols. per 1000 grams of solution. The solutions were treated similarly, and it is shown that the stable solid phases are  $\text{NH}_4\text{H}_2\text{PO}_4$ ;  $(\text{NH}_4)_2\text{HPO}_4$ ; and  $(\text{NH}_4)_3\text{PO}_4 \cdot 3\text{H}_2\text{O}$ . The four-component system, potassium hydroxide, ammonia, phosphoric acid, and water was then investigated in the same way. A solution containing all four substances was then placed over sulphuric acid and allowed to remain there until it ceased to lose weight, that is, until the point of lowest vapour pressure was reached. The solid which had separated and the solution were then analysed, the latter containing 1.81 mols.  $\text{NH}_3$ , 4.95 mols. K, and 3.96 mols. of  $\text{PO}_4$  per 1000 grams of solution. The solid was shown by optical examination to contain  $\text{KH}_2\text{PO}_4$  and  $\text{K}_2\text{PO}_4$ , whilst ammonia was rapidly evolved. It is shown that to produce a stable compound of the type desired, it will be necessary to employ more acid solutions than those used here. J. F. S.

**Structural Changes in Industrial Brasses.** DOMENICO MENEGHINI (*Ann. Chim. Applicata*, 1914, 2, 154—158).—The brass parts of incandescent gas burners were found to become very brittle, and, in some cases, to fracture spontaneously. Analysis revealed no change in the composition of the brass, which contained 64.5% of copper, 35.0% of zinc, 0.3—0.4% of lead, and traces of iron. Micrographical examination showed that the majority of the specimens consisted solely of the homogeneous  $\alpha$ -solution, although in a few instances traces of  $\beta$ - and  $\gamma$ -solutions were observed; no sign of the polyhedral structure noticed in analogous cases was detected. After the fragments of brass were reheated at  $700^\circ$ , they were found to have undergone a marked diminution in the superficial hardness, such diminution varying from point to point of one and the same fragment. These effects are probably the result of, first, the mechanical treatment to which the metal is subjected during the shaping of the parts, and, secondly, electrolytic action due to the sulphur dioxide formed during the combustion of the gas and to moisture. In order to avoid the so-called "Forrier-Krankheit," that is, the formation of internal tensions caused by the heating of brass which has been worked below its final temperature of solidification, the metal should contain at least 70% of copper. Even with such alloys, consisting entirely of the  $\alpha$ -solution, trouble may occur unless, after they have attained their final shape, they are rendered stable by suitable reheating. T. H. P.

**The System: Copper Sulphate, Copper Chloride, Potassium Sulphate, Potassium Chloride, and Water at  $30^\circ$ .** F. A. H. SCHREINEMAKERS and (MISS) W. C. DE BAAT (*Proc. K. Akad. Wetensch. Amsterdam*, 1914, 17, 533—545).—The corresponding systems containing ammonium and sodium in place of potassium have been described in previous papers (A., 1909, ii, 403; 1911, ii, 592). In the present case the solubility data indicate that the solid phases occurring at  $30^\circ$  are the simple salts  $\text{K}_2\text{SO}_4$ ,  $\text{KCl}$ ,  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  and  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ , the double salts  $\text{K}_2\text{SO}_4 \cdot \text{CuSO}_4 \cdot 6\text{H}_2\text{O}$ ,  $2\text{KCl} \cdot \text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ .

# ABSTRACTS OF CHEMICAL PAPERS.

and a salt corresponding with the formula  $K_2SO_4 \cdot CuCl_2 \cdot 6H_2O$ , which sometimes separates in combination with one molecule of water and at other times in the anhydrous condition. The spatial model which serves to represent the equilibrium relationships is accordingly characterised by seven surfaces of saturation, each one of which corresponds with one or other of the above-mentioned solids. In addition, it has been found that a substance of the composition  $6KCl \cdot 2CuSO_4 \cdot 7H_2O$  sometimes separates out as a metastable phase.

Data showing the composition of solutions saturated with respect to one, two, and three solid phases are recorded in a series of tables.  
H. M. D.

**The Stokes Method for the Determination of Pyrite and Marcasite.** E. T. ALLEN and J. I. CRENSHAW (*Amer. J. Sci.*, 1914, [iv], **36**, 371—392).—Stokes' method (A., 1902, ii, 87) has been used in connexion with the authors' work on the artificial production of crystallised forms of iron sulphide (A., 1911, ii, 1093; 1912, ii, 354). The details of the method and its limitations are here stated more fully.  
L. J. S.

**Effect of Temperature and Acidity in the Formation of Marcasite and Wurtzite.** E. T. ALLEN and J. I. CRENSHAW; with Microscopic Study by H. E. MERWIN (*Amer. J. Sci.*, 1914, [iv], **36**, 393—431).—The authors' earlier results on the formation of the unstable forms (marcasite and wurtzite respectively) of iron sulphide and zinc sulphide (A., 1912, ii, 354, 1055) have been re-investigated and confirmed, and new data determined.  
L. J. S.

**Constitution of Aluminates.** II. EDWARD G. MAHIN (*J. Amer. Chem. Soc.*, 1914, **36**, 2381—2383).—The author criticises Blum's paper (A., 1913, ii, 963), and maintains the accuracy of the view expressed by Mahin, Ingraham, and Stewart (A., 1913, ii, 139) that the solubility of aluminium hydroxide in alkali hydroxide solutions is due rather to its colloidal properties than to the formation of salts.  
E. G.

**Constitution of Aluminates.** WILLIAM BLUM (*J. Amer. Chem. Soc.*, 1914, **36**, 2383—2384).—In reply to Mahin (preceding abstract) the author advances certain considerations in justification of his contention that definite aluminates of the composition  $MAO$  probably exist in aqueous solution.  
E. G.

**Behaviour of Ammonium Phosphomolybdate with Ammonium Hydroxide.** PULIN BIHARI SIRCAR (*J. Amer. Chem. Soc.*, 1914, **36**, 2372—2374).—Gibbs (A., 1884, 560, 713) has shown that a solution of ammonium phosphomolybdate in ammonia deposits crystals of the compound  $2(NH_4)_3PO_4 \cdot 5MoO_3 \cdot 7H_2O$ .

It has now been found that when excess of solution of ammonia (D 0.91) is added to a solution of ammonium phosphomolybdate, heat is

veloped, and a white, crystalline salt,  $(\text{NH}_4)_2\text{Mo}_2\text{O}_7 \cdot 3\text{NH}_3$ , is produced, which gradually loses ammonia. If more dilute ammonia (D 0.92) is employed, a precipitate is not formed, but a solution is obtained which on evaporation yields crystals of the compound  $(\text{NH}_4)_2\text{Mo}_2\text{O}_7 \cdot 3\text{NH}_3$ ; the salt described by Gibbs is but seldom obtained. When ammonium phosphomolybdate is treated with a large excess of strong solution of ammonia (D 0.90), the crystalline precipitate is first produced, and, on further addition of ammonia, dissolves to form a solution from which a gelatinous substance separates; the latter compound,  $(\text{NH}_4)_2\text{HPO}_4$ , is very hygroscopic. Ordinary ammonium molybdate was found to have the composition  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ . E. G.

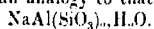
## Mineralogical Chemistry.

**Rubidium Microcline.** V. I. VERNADSKI (*Bull. Soc. Franç. Min.*, 1913, **36**, 258—265. Compare A., 1911, ii, 122).—Analysis of the bluish-green microcline (Amazon-stone) from the Ilmen Mountains, Urals, showed the presence of 3.12%  $\text{Rb}_2\text{O}$ , corresponding with 10.89% of the silicate  $\text{Rb}_2\text{Al}_2\text{Si}_6\text{O}_{16}$ . Spectroscopic examination of orthoclases from the neighbourhood of Mursinka, Urals, suggested the presence of even larger amounts of rubidium. The very frequent presence of rubidium and cesium in potash-feldspars and in micas accounts for the wide distribution of these elements in the earth's crust and in sea-water. L. J. S.

**Searlesite, a New Mineral.** ESFER S. LARSEN and W. B. HICKS (*Amer. J. Sci.*, 1914, [iv], **38**, 437—440).—This new mineral was washed from a sample of clay from a boring at Searles Lake, San Bernardino Co., California. It has the form of small, white spherulites, which are composed of radial fibres, the optical characters of which suggest monoclinic symmetry. The mineral is rather soft, and fuses below red-heat to a nearly clear glass. It is readily decomposed by hydrochloric acid, and is appreciably soluble in water. The optical constants show a gradual change when the material is treated with acids. Analysis of the impure material gave I, and deducting  $\text{CaCO}_3$  (present as calcite) 21.63%,  $\text{MgCO}_3$  6.41%, insoluble (quartz, feldspar, chlorite, etc.), and hygroscopic water, these results are re-calculated under II:

	$\text{Na}_2\text{O}$	$\text{B}_2\text{O}_3$	$\text{Na}_2\text{O}$	$\text{K}_2\text{O}$	$\text{CaO}$	$\text{MgO}$	$\text{FeO}$	$\text{Al}_2\text{O}_3$	$\text{H}_2\text{O}$	$\text{H}_2\text{O}$	$\text{CO}_2$	Insol.	Total.
I.	21.00	9.80	7.70	0.60	12.10	4.20	1.14	0.22	5.72	0.78	12.84	11.98	100.08
II.	56.41	16.26	12.78	1.60	—	1.82	1.89	0.37	9.47	—	—	—	100.00

The formula  $\text{Na}_2\text{O} \cdot \text{B}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot 2\text{H}_2\text{O}$  when written in the form  $\text{NaB}(\text{SiO}_3)_2 \cdot \text{H}_2\text{O}$  shows an analogy to that of analcite,



L. J. S.

**The Decomposition Products of Aluminium-containing Siliceous Rocks, and in Particular of the Laterites of Madagascar.** A. Lacroix (*Compt. rend.*, 1914, 159, 617-622. *Compt. Rend. Acad. Muséum*, 1913, 5, 255).—A comparison of the rock formations in Madagascar and French Guinea, and the change which these rocks undergo on weathering. In Madagascar the surface of the land is covered by red earth, and not by a rock crust, although the latter is visible in places. There is an absence of the specialisation in the manner of weathering according to the nature of the original rock, which was found in Guinea. The diabbases, basalts, and syenites decompose, giving gibbsitic laterites. Total transformation also occurs, in some cases, into colloidal aluminium silicate and colloidal aluminium hydroxide, this mode of decomposition being seldom, if ever, found in Guinea. The gneisses, mica-schists, and granites, forming the greater part of the central rock system, most frequently decompose, giving a mixture of aluminium silicate and hydroxide. This is the change which occurs in most of the red earths. In one place bauxitic laterite was found comparable to that of the African zone of concretion. A further change, taking place at the expense of the granite and the pegmatite, yields a kaolin identical with that of temperate climates, but sometimes containing a little free aluminium hydroxide and some colloidal aluminium silicate. A final method of decomposition, not observed in Guinea, consists in the production of a gibbsitic laterite, comparable to that from the diabbases, except that the unattacked quartz remains, and owing to the extreme poverty in iron, or even its absence, these laterites are very light in colour, and sometimes even quite white. A point worthy of note is that the same rock, for example, pegmatite, undergoes different methods of decomposition at the same altitude and in localities only a few kilometres apart and under similar conditions. No satisfactory explanation is at present given of this difference. The author states that the red earths of Madagascar are improperly called laterites, and should rather be named lateritic clays. W. G.

**Hydrographical Chemistry. Relation Between the Different Salts in Sea-Water.** A. MASUZZI (*Ann. Chim. Applicata*, 1914, 132-153).—The author gives a summary of the literature dealing with the saline composition of sea-water and with the method suggested for calculating the total salinity from the proportion of one constituent ion, for example, chlorine. A description is given of the work carried out by Sørensen (*Mém. Acad. Roy. Sci. Let. Danemark*, 1902, [vi], 12, No. 1). The statement made by various investigators that no constant relations exist between the proportions of the different constituents of sea-water has been controverted by Ruppin (*A.*, 1911, ii, 123), who demonstrated, in particular, the constancy of the ratio, sulphate to chloride. Ruppin examined only two samples of water from the Mediterranean, and the author has now extended the investigation to a number of other samples from the Mediterranean and Adriatic Seas. The mean value of the ratio  $100\text{SO}_4 : \text{Cl}$  is found to be 11.614, the maximum diver-

ice being  $+0.041$  to  $-0.029$ ; Ruppin's value is  $11.597$ . Waters collected near the mouths of rivers naturally show varying values for this ratio.

T. H. P.

### Analytical Chemistry.

**Weighing Burette.** H. S. BAILEY (*J. Ind. Eng. Chem.*, 1914, 6, 41). A burette for weighing out quantities of such liquids as oils, etc., consists of a graduated glass tube holding about 30 c.c.; the top of the tube is closed with a stopper, and the lower end is narrowed and then drawn out to a jet. This jet is closed by a glass rod which passes through a hole in the stopper and extends down to the centre of the tube, the bottom of the rod being ground into the jet. The lower narrow part of the tube is also ground on its exterior, and fits into a small glass foot, so that the apparatus may stand on the balance pan. To discharge a portion of the contents of the tube the latter is removed from the foot and the centre rod is used slightly.

W. P. S.

**Methods for Extractions by means of Immiscible Solvents from the Point of View of the Distribution Coefficients.** [J. W. MARDEN and VANNA ELLIOTT (*J. Ind. Eng. Chem.*, 1914, 6, 28-934. Compare this vol., ii, 483). The distribution coefficients of a number of substances have been investigated with a view to ascertaining the best conditions under which to make extractions. It is shown that chloroform is a better substance than ether for the extraction of aconitine and codeine from their aqueous solutions. Chloroform is also a better solvent for strychnine than mixtures of chloroform and ether, whilst ether answers well for the extraction of cocaine. The distribution of citral between lemon oil and 45% and 50% alcohol is discussed; the latter strength of alcohol yields the better results, since 90% of the citral is extracted when 1 volume of the oil is shaken with 18 volumes of 50% alcohol. A rapid method has been devised for the extraction of morphine, but a use of the distribution ratio is suggested in order to avoid continued extractions.

W. P. S.

**Method for Preparing a Neutral Ammonium Citrate Solution.** J. M. McCANDLESS (*J. Ind. Eng. Chem.*, 1914, 6, 921-922).—The citric acid to be employed is well mixed and ground, and a weighed portion of 0.35 gram is titrated with  $N/10$  alkali hydroxide solution, using phenolphthalein as the indicator; if the acid is pure and uneffloresced, exactly 50 c.c. of the alkali solution will be required. One thousand eight hundred and fifty grams of the pure acid, or its equivalent in effloresced or impure acid, are then placed in a large stoppered bottle, dissolved in about 7 litres of water, and

a quantity of ammonia is added in the ratio of 1 part by weight actual ammonia to 3.765 parts of anhydrous citric acid. The ammonia solution added must be titrated previously, using methyl orange as indicator, and may be used in the form of the concentrated solution or after dilution; in the latter case less water employed to dissolve the citric acid. The mixture is shaken until any remaining citric acid is dissolved, cooled, and diluted D 1.09. The volume of the resulting solution is about 10 lit. The accuracy of the solution may be confirmed by the distillat method, by the method described by Patten and Marti (A., 1913, 790), or by that of Eastman and Hildebrand (this vol., ii, 675).  
W. P. S.

**Accuracy of Neumann's Method for the Estimation of Phosphorus.** H. S. HALCRO WARDLAW (*J. Roy. Soc. New South Wales*, 1914, 48, 73—93).—The results obtained in the estimation of phosphoric acid by Neumann's method (A., 1903, ii, 243; 1905, 68) are always too high, the error increasing with the amount of phosphate present. The application of the method to pure phosphates and to milks shows that when dealing with 22 mg. of phosphoric acid ( $P_2O_5$ ) the average error is +4%. The error is due to excess of molybdenum carried down with the ammonium phosphomolybdate precipitate; it does not depend on the rate of addition of the precipitant or on the time of contact of the precipitate with the mother liquor. To ensure complete precipitation of the phosphoric acid, it is necessary to make the precipitation at 70—80°C. The error cannot be eliminated by lowering the temperature; this leads to incomplete precipitation.  
W. P. S.

**Rapid and Accurate Method for the Estimation of Carbon in Iron and Its Alloys.** ERNST SZÁSZ (*J. Soc. Chem. Ind.*, 1914, 994—997. Compare A., 1913, ii, 621).—The apparatus described previously is modified. An electrical crucible furnace is employed and the boat containing the iron is placed in one end of a porcelain tube which is open at both ends. This tube is surrounded by a similar, slightly larger tube closed at the end which is placed in the furnace; the space between the two tubes may contain a mixture of cobalt oxide and fire-clay. The outer ends of the tubes are connected by a stuffing-box, and surrounded by a cooling jacket. The oxygen is supplied to the outer end of the inner tube, and the combustion gases leave the apparatus by a side-tube on the outer porcelain tube, and are conducted to the gas-measuring apparatus or to an absorption vessel. Dilute sulphuric acid (1 : 10) is used in place of mercury in the gas-measuring burette. Both the method and apparatus are patented.  
W. P. S.

**Properties of Some Calcium and Magnesium Salts, and their Bearing on the Quantitative Separation of these Metals.** C. BLOMBERG (*Chem. Weekblad*, 1914, 11, 1002—1008).—A criticism of the methods recommended for the separation of calcium and magnesium. The author condemns the method of crystallising magnesium oxalate recommended by Jannasch.

method of Hefelman and of Richards, the cold precipitation and the double precipitation methods of Fresenius, and the method involving the solution of magnesium oxalate by addition of excess oxalate. A. J. W.

**Rapid Methods for Glass Analysis.** E. C. SULLIVAN and W. C. RYAN (*J. Ind. Eng. Chem.*, 1914, 6, 897-899).—A method for the analysis of glass containing silica, lead, sodium, potassium, and all quantities of iron, aluminium, calcium, and magnesium, consists in decomposing the glass with hydrofluoric acid, the oxides in turn being decomposed by oxalic acid. One gram of powdered glass is treated with hydrofluoric acid and 2 grams of oxalic acid, the mixture is evaporated to dryness, and heated sufficiently to expel the excess of oxalic acid; this evaporation with oxalic acid (and water) is twice repeated. The residue of oxalates treated with hot water, cooled, and filtered; the insoluble portion consists of lead oxalate, with a trace of calcium oxalate, and the residue may be estimated as sulphate. The filtrate from the lead oxalate is evaporated to dryness, the residue is ignited to decompose the oxalates, dissolved in hydrochloric acid, and the solution employed for the estimation of the bases. If arsenic and antimony are present, they must be removed from the soluble oxalates by treatment with hydrogen sulphide before the oxalates are decomposed.

In the case of borosilicate glasses the boric acid may be estimated by the method described by Wherry (*A.*, 1909, ii, 92), but trustworthy results are obtained when the glass also contains lead and calcium unless the method is modified as follows: 0.5 gram of the glass is fused with 3 grams of sodium carbonate, the mass is treated with water, and the solution filtered. About 7 c.c. of concentrated hydrochloric acid are added to the filtrate, the solution is heated to boiling, and excess of calcium carbonate is introduced, the excess being then continued as described by Wherry. W. P. S.

**Sulphate Method for Standardising a Magnesium Salt Solution.** C. W. FOULK and O. R. SWEENEY (*J. Amer. Chem. Soc.*, 1914, 36, 2360-2372).—In the course of an investigation into the causes of the discrepancies in the results obtained in the precipitation of magnesium as magnesium ammonium phosphate by different methods and by different workers, a study was made of the precipitation and standardisation of a solution of a magnesium salt. A sample of magnesium chloride, which contained sodium, was purified by precipitating the magnesium as magnesium ammonium phosphate (Bray, *A.*, 1909, ii, 431), converting this into magnesium ammonium chloride, and heating the latter in a current of dry hydrogen chloride. Weighed quantities of the anhydrous magnesium chloride thus obtained were converted into the sulphate. In order to accomplish this operation, a special form of apparatus was devised, which enables a substance to be heated in a combustion flask and transferred to a weighing bottle without exposure to the air. Six experiments were made on the conversion of the anhydrous chloride into the sulphate, and the results obtained













